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A TEXTBOOK OF PURE AND APPLIED CHEMISTRY

83

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BY

JAMES E. GARSIDE

Ph.D. (Lond.), M.Sc.Tech. (Manc.), F.R.I.C., F.I.M.

(*Head of Department of Applied Chemistry, Northampton Polytechnic, London, E.C.1*)

AND

R. F. PHILLIPS

M.A., B.Sc. (Oxon.), Ph.D. (Lond.), F.R.I.C.

(*Head of Department of Pure and Applied Science and Chemical Engineering, The Loughborough College of Technology*)

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PREFACE

It has been the aim of the authors to present an account of the more important aspects of general chemistry in a form suitable for use by students taking various courses and studying different aspects of both pure and applied chemistry. Some of the chemistry courses which the authors have had in mind throughout, and for which this book may be used to advantage, include National Certificate courses; applied chemistry courses such as those in metallurgy, metal finishing, fuel technology, chemical engineering and ceramic technology, in all of which chemistry plays a predominant part; chemistry courses for the General Certificate of Education at both the Ordinary and Advanced levels; Intermediate Science and Subsidiary Chemistry for degree courses. It is also recommended to those engineers who are anxious both to acquire a working knowledge of chemistry and also to become conversant with the variety of new materials and processes which characterize this present age.

Although limitations of space have prevented the authors from dwelling in any detail on the history of chemistry, it should not be construed from this that they consider the historical approach of little value. Indeed, they would urge all sincere students of chemistry to take every opportunity to learn of, and profit from, the difficulties and triumphs experienced by those who, from the time of the alembic to this radiochemical age, have made scientific integrity a principle of life. It is perhaps appropriate, therefore, to direct the reader's attention to the Chemical Society's series of Memorial Lectures in which are given accounts of the lives and works of many distinguished chemists of all nationalities.

In preparing the manuscript the authors have been able to consult many authorities and every effort has been made to give acknowledgment in the text where appropriate. In addition a number of industrial organizations have most kindly permitted reproduction of their illustrations. To these, the authors wish to express their appreciation and thanks and would also like to apologize in advance for any acknowledgment inadvertently omitted.

J. E. G.

R. F. P.

September, 1952

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PART I

GENERAL THEORETICAL AND PHYSICAL CHEMISTRY

By

JAMES E. GARSIDE, Ph.D., M.Sc.Tech., F.R.I.C., F.I.M.

CHAPTER 1

THEORETICAL BACKGROUND OF CHEMICAL COMBINATION

ALL known substances are characterized by certain specific and constant properties, chemical and physical, which permit of their classification into one or other of several groupings. For example, certain substances are incapable of being broken down into simpler substances either by physical methods or as the result of the ordinary types of chemical reaction. Such simple substances are known as *elements*.

On the other hand, by the application of physical processes or of chemical reactions, many substances may be split up into two or more simpler substances. If this division into simpler substances may be effected by the employment of physical means the initial substance is known as a *mixture*. If, however, in order to effect subdivision a chemical reaction is necessary, then the initial substance is termed a *compound*.

Granite is a mixture, the chief component substances of which are quartz, felspar and mica. Each of these individual component substances exhibits a number of specific properties and the chief characteristic of a mixture is that each of the component substances exhibits precisely the same properties as it would were it existing alone, since in admixture it is unaffected by the presence of the other components. In other words, specific properties are not destroyed by mixing.

Salt is an example of a compound formed by the chemical combination of the two elements sodium and chlorine, a compound being defined as *a substance resulting from the synthesis of, and capable of decomposition by means of a chemical reaction into, two or more simpler substances.*

If zinc powder is mixed with powdered sulphur there is produced a mixture from which the sulphur may easily be separated again from the zinc by taking advantage of a property of sulphur, namely its solubility in carbon disulphide, in which zinc is insoluble. If, however, this mixture of zinc powder and powdered sulphur is heated to dull red heat an entirely new substance, zinc sulphide, is formed. Zinc sulphide is an example of a compound and it is impossible by the use of the solvent carbon disulphide to extract or dissolve out the sulphur since this element is now chemically combined with the zinc as zinc sulphide. Similarly, if a mixture of zinc powder and powdered sulphur is treated with a little dilute hydrochloric acid, the zinc reacts with the acid to give rise to the evolution of the odourless gas hydrogen, whereas when zinc sulphide is treated with hydrochloric acid in the same way this compound gives rise to the evolution of a strongly

smelling gaseous compound, hydrogen sulphide, instead of the gaseous element hydrogen. Thus, the synthesis of zinc sulphide from its component elements zinc and sulphur has resulted concurrently in the loss of the individual properties of the elements zinc and sulphur and the appearance of the different properties of zinc sulphide.

CHEMICAL COMBINATION BY WEIGHT

The formation of chemical compounds from their component elements is governed by four laws.

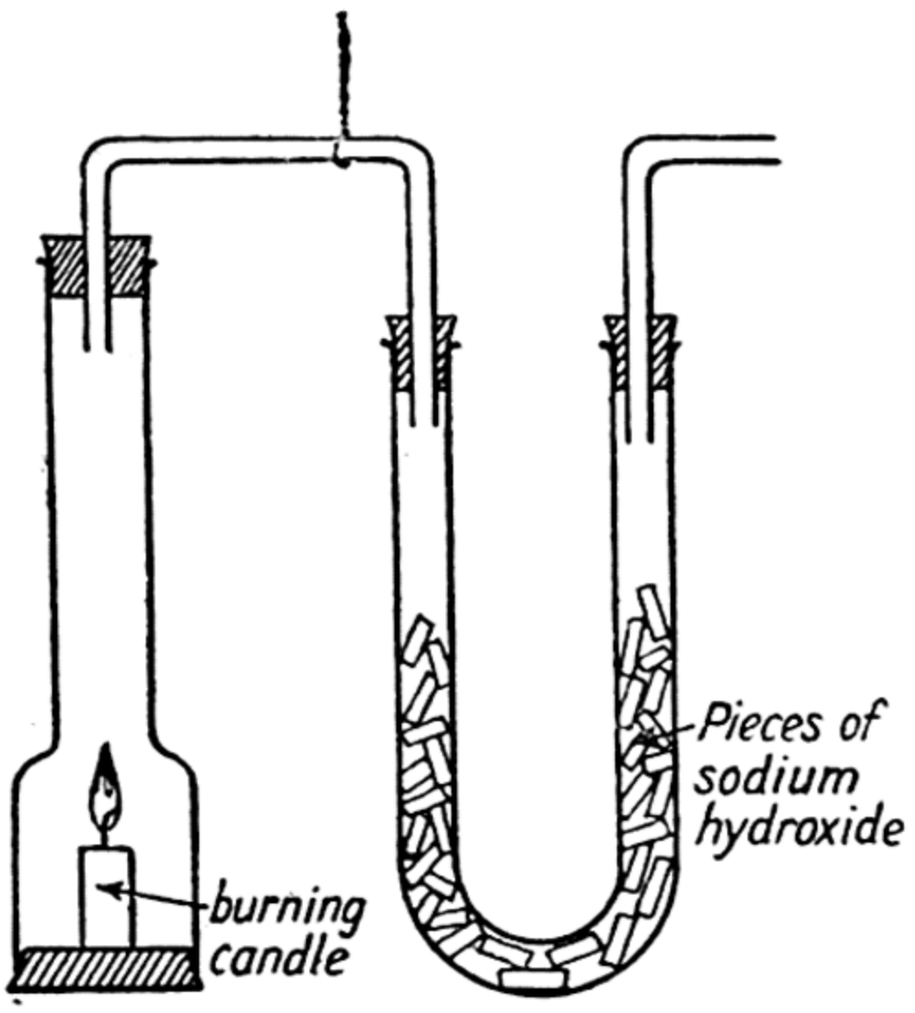

FIG. 1. Law of Conservation of Mass illustrated by the Burning of a Candle

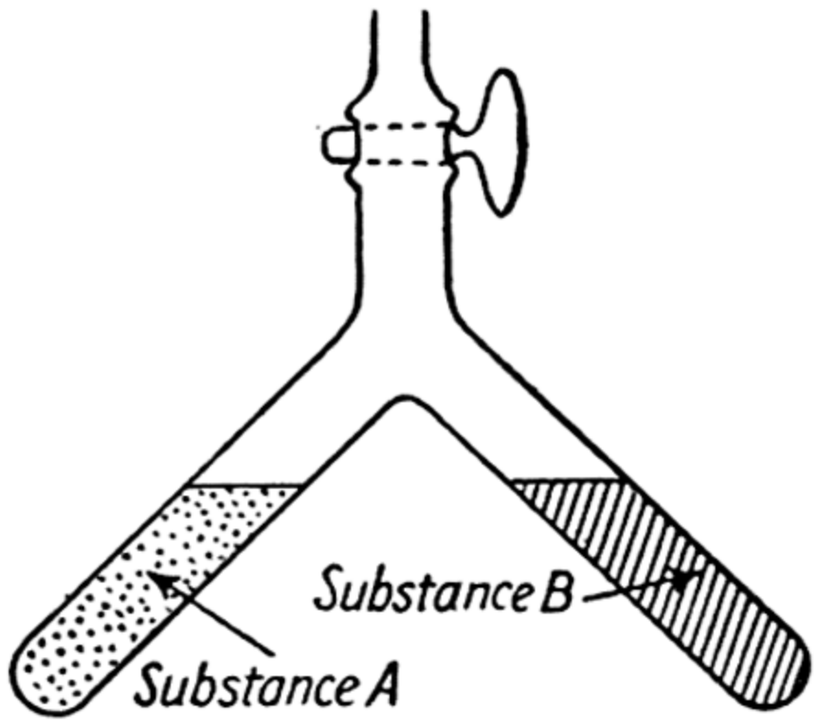

FIG. 2. Reaction to illustrate the Law of Conservation of Mass

The Law of Conservation of Mass

This law is the basis of all quantitative chemistry and states that *the total mass of a system is unaffected by any chemical change which may occur within the system.**

The validity of this law may be demonstrated by the combustion of the candle within the apparatus as shown in Fig. 1. The candle slowly disappears by combustion but the total weight of the apparatus, suspended on the balance beam, remains constant since the gaseous products of the combustion are absorbed by the sodium hydroxide contained within the U tube, i.e. total weight of reactants = total weight of products.

* Strictly applied this statement implies that matter can neither be created nor destroyed in a chemical reaction, and is sometimes called *The Law of Indestructibility of Matter*. This, however, is not in accordance with relativity theory which requires that matter is regarded as partly convertible into energy as a result of a chemical reaction. Since the loss of mass in any given small scale chemical experiment is extremely small, the law of conservation of mass remains to all intents and purposes a correct statement of practical experience.

Similarly, reactions in solution between substances contained within closed vessels such as is shown in Fig. 2 afford confirmation of the validity of this law. Typical pairs of substances suitable to serve as reactants are ferrous sulphate and silver sulphate, and iodine and sodium sulphite.

The Law of Constant Proportions

This law states that *a chemical compound always has the same, fixed composition by weight.* It may be illustrated by reference to the compound, black copper oxide. This compound, which consists solely of the two elements copper and oxygen, may be prepared by heating any one of the compounds, copper carbonate, copper nitrate, or copper hydroxide. No matter which compound is selected the black copper oxide thus produced always has the same percentage composition by weight of copper and oxygen.*

The Law of Multiple Proportions

This law states that *when two chemical elements combine together in more than one proportion* (*forming two or more compounds*), *the weights of one element which unite with a fixed weight of the other element are in a simple ratio.* This law may be illustrated by reference to the two oxides of carbon, i.e. carbon monoxide and carbon dioxide. It has been shown as the result of very precise investigations that in the formation of carbon monoxide, 1 g of carbon combines with 1·3333 g of oxygen; whilst in the case of carbon dioxide, 1 g of carbon combines with 2·6666 g of oxygen. Thus, the ratio of the two combining weights of oxygen in the two different oxides of carbon is 1·3333 : 2·6666, that is, 1 : 2. Similarly, in the case of the five oxides of nitrogen—nitrogen monoxide, dioxide, trioxide, tetroxide and pentoxide—a similar condition prevails in that 1 g of nitrogen combines with weights of oxygen in the ratio of 0·572 : 1·144 : 1·716 : 2·288 : 2·850 g, i.e. in the ratio of 1 : 2 : 3 : 4 : 5.

The Law of Reciprocal Proportions

This law, which is also known as the *Law of Equivalent Proportions* is as follows: *The different weights of two elements which react separately with a constant weight of a third element bear a simple ratio to the proportions by weight in which they will react with one another, or with a fourth element.*

Thus, for example in hydrochloric acid, each 1 g of hydrogen is combined with 35·5 g chlorine, and when this acid is acted upon by metallic magnesium, 1 g of hydrogen is liberated by each 12 g of the metal. According to the statement of the Law of Reciprocal Proportions, when magnesium

* It is to be noted here that the discovery of isotopes has rendered invalid the universal application of this law. The implications of this fact will be discussed later (*see* p. 55).

and chlorine combine they should do so in the proportion of 12 g of magnesium with 35·5 g of chlorine, and this is shown to be the case since in magnesium chloride 24 g of magnesium combine with 71 g of chlorine, or 12 g magnesium with 35·5 g of chlorine.

THE ATOMIC THEORY

A quantitative interpretation of the four laws of chemical combination described above is provided by the Atomic Theory, first proposed more or less in its modern form by John Dalton in his well-known *New System of Chemical Philosophy* (Manchester, 1808–10).

The essential points of Dalton's Atomic Theory are—

(*a*) All elements are composed of discrete particles known as *atoms*, an atom being defined as the smallest particle of an element which may take part in a chemical reaction.

(*b*) All atoms of any one element are alike in weight, and in all other properties, and differing in these respects from the atoms of other elements.

(*c*) Resulting from chemical reaction, atoms of different elements may combine together to form *molecules* of chemical compounds in the production of which the union of atoms occurs in a simple numerical ratio. A molecule is defined as the smallest portion of a substance (which may be either a chemical compound or a chemical element) capable of individual existence. It is to be noted here that in the case of a molecule of a chemical compound the atoms of the elements which make it up are dissimilar, whereas in the case of a molecule of an element the atoms are all similar to one another.

Since the absolute weight of a single atom of any element is of very small magnitude it is usual to express the atomic weight of an element by reference to the atomic weight of some other element chosen as standard. Thus, the atomic weight of an element is the ratio of the weight of an atom of that element to the weight of an atom of a standard element. In the true sense, therefore, the atomic weight as normally quoted is not a weight but a ratio. Originally hydrogen was chosen as the standard element with an atomic weight of unity. On this basis, oxygen has an atomic weight of 15·875. However, it was observed that only about half of the elements formed compounds with hydrogen, whilst with oxygen they nearly all formed compounds which were very suitable for analysis, and hence for atomic weight determination. It has, therefore, been agreed internationally that atomic weights shall be evaluated on the basis of oxygen as the standard element with an atomic weight of 16.

A further simplification which accrues from the adoption of oxygen as standard is that the atomic weights of a number of elements approach more closely to whole numbers than they do when hydrogen is taken as the standard element. On the basis of oxygen as 16·000, the atomic weight of hydrogen is 1·0078.

THE GAS LAWS AND MOLECULAR THEORY

Variations in temperature, with or without pressure variations, and the onset of chemical reactions, give rise to corresponding changes in the volume of gases. There are four laws which relate the behaviour of gases under the influence of such variables. These laws are—

(*a*) Boyle's Law,
(*b*) Charles's Law,
(*c*) Dalton's Law of Partial Pressures, and
(*d*) Gay-Lussac's Law of Volumes.

Boyle's Law (1662)

This law, sometimes known as Mariotte's Law, states that, *provided the temperature remains constant, the volume of a given mass of gas varies inversely as the pressure exerted upon it*, i.e. for any given temperature,

$$V \propto \frac{1}{P}$$

or

$$PV = k_1 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P = pressure, V = volume of a given mass of the gas, and k_1 = a constant.

Charles's Law (1802)

This law, derived by Gay-Lussac following earlier experiments by Charles, states that, *provided the pressure remains constant, the volume of a given mass of a gas is directly proportional to its temperature as measured on the absolute temperature scale*, i.e. at any given pressure,

$$V \propto T$$

or

$$V = k_2 T \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where V = volume of a given mass of the gas, T = temperature of the gas on the absolute scale, and k_2 = a constant.

These two laws may be combined in the single statement that the product of the pressure and the volume of a given mass of a gas is proportional to the temperature of the gas on the absolute temperature scale. This may be expressed mathematically in a single equation, thus—

$$PV = k_3 T \quad . \quad . \quad . \quad . \quad (3)$$

where P, V and T have the same significance as in equations (1) and (2), and k_3 is a constant involving both k_1 and k_2.

The numerical value of the constant k_3 will be dependent upon the mass of gas involved.

If this mass is the molecular weight in grammes (i.e. the gramme molecular weight or gramme molecule, or more simply the mole) then k_3 will

assume a particular value, being the same for all gases. This particular value is denoted by using in place of k_3 the symbol R, which is termed the *gas constant*. The numerical value of the gas constant is independent of the nature of the substance under examination, or of the physical conditions which exist. Equation (3) then assumes the form—

$$PV = RT \quad . \quad . \quad . \quad . \quad (4)$$

being known as the *equation of state* for the mole.

The general equation of state applying to any mass of gas is—

$$PV = nRT \quad . \quad . \quad . \quad . \quad (5)$$

where n = number of moles of the gas, other symbols retaining their previous significance.

Numerical Value of the Gas Constant. At 0°C (i.e. 273°K) and 1 atmosphere (i.e. 760 mm) pressure one mole of any gas occupies 22·41 litres. Applying equation (4) the numerical value of the gas constant is—

$$R = \frac{PV}{T}$$

$$= \frac{1 \times 22{\cdot}41}{273}$$

$$= 0{\cdot}08207 \text{ litre-atmospheres/mole/°K}$$

However, since a pressure of one atmosphere will maintain a column of mercury (density = 13·59) 76 cm high under a force due to gravity of 981 cm/sec² and—

$$1 \text{ litre-atmosphere} = 1000 \times 13{\cdot}59 \times 76 \times 981 \text{ ergs}$$
$$= 101{\cdot}3 \times 10^7 \text{ ergs}$$

therefore, $R = 0{\cdot}08207$ litre-atmospheres

$$= 8{\cdot}314 \times 10^7 \text{ ergs/mole/°K}$$

However, $1 \text{ joule} = 1 \times 10^7$ ergs

therefore, $R = 8{\cdot}314$ joules/mole/°K

and since, $1 \text{ calorie} = 4{\cdot}185 \times 10^7$ ergs

then, $R = 1{\cdot}986$ calories/mole/°K

Dalton's Law of Partial Pressures (1801)

This law, which states that *the sum of the partial pressures of the constituent gases of a mixture of gases is equal to the total pressure of the gas mixture*, illustrates further the mutual independence of the molecules of a gas.

Gay-Lussac's Law of Volumes (1808)

Dalton proposed that in the process of chemical reactions the union of atoms occurred in a simple numerical ratio whilst Gay-Lussac pointed out

that gases react in simple proportions by volume. This is expressed more precisely in Gay-Lussac's Law of Volumes which states that *when gases combine chemically, the volumes of gases which react and the volumes of their products, if gaseous, bear a simple relation to one another when measured under the same conditions of temperature and pressure.*

Thus, in the formation of hydrogen chloride from the component elements hydrogen and chlorine, equal volumes of the elemental gases unite to form two volumes of gaseous hydrogen chloride—

$$\underset{1\text{ volume}}{\text{Hydrogen}} + \underset{1\text{ volume}}{\text{Chlorine}} = \underset{2\text{ volumes}}{\text{Hydrogen chloride}}$$

Similarly, in the formation of water from the elemental gases hydrogen and oxygen, 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of water (this compound being measured in the form of water vapour).

$$\underset{2\text{ volumes}}{\text{Hydrogen}} + \underset{1\text{ volume}}{\text{Oxygen}} = \underset{2\text{ volumes}}{\text{Water (as water vapour)}}$$

At first, Gay-Lussac, Dalton, and others tried to show that the Law of Volumes demonstrated that, under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of atoms. This assumption, however, leads to an absurdity, as is shown by the following discussion.

2 volumes of hydrogen + 1 volume of oxygen = 2 volumes water vapour

Suppose each volume of hydrogen contains n atoms of hydrogen, then,

$2n$ atoms of hydrogen + n atoms of oxygen = $2n$ particles of water vapour

and,

2 atoms of hydrogen + 1 atom of oxygen = 2 particles of water vapour

These two particles of water vapour must be identical, each containing one atom of oxygen. But this is obviously absurd since there is available only one atom of oxygen and by definition an atom is incapable of sub-division by chemical means.

AVOGADRO'S HYPOTHESIS

The difficulty described above was overcome by Avogadro who proposed that *under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules.* This statement is usually known as Avogadro's Hypothesis. The molecules of all the elements contain one or more atoms, usually a small whole number of atoms. The number of atoms present in a molecule of an element is known as the *atomicity* of the element.

Deductions from Avogadro's Hypothesis

The Atomicity of Hydrogen (and certain other gases). A study of the volume relationships of hydrogen and chlorine when they react together to form hydrogen chloride leads to the fact that

1 volume of hydrogen reacts with 1 volume of chlorine to produce
2 volumes of hydrogen chloride

Thus, from Avogadro's Hypothesis it follows that

1 molecule of hydrogen reacts with 1 molecule of chlorine to produce
2 molecules of hydrogen chloride

Since two molecules of hydrogen chloride have thus been produced from one molecule of hydrogen and one molecule of chlorine, each molecule of hydrogen (and of chlorine) must be capable of subdivision into two equal parts, in other words each molecule of hydrogen must contain an equal number of hydrogen atoms. By a similar argument it may be established that the chlorine molecule also contains an equal number of chlorine atoms. Now hydrogen is a gas which reacts with other elements forming a large number of gaseous compounds, of which some at least must contain only one atom of hydrogen. It has been shown by experiment that the weight of hydrogen in a fixed volume (e.g. one litre at S.T.P.*) in any one of these gaseous hydrogen compounds is never less than a certain minimum value which must therefore correspond to the presence of a single atom of hydrogen in a molecule of the compound. Since experiment has also shown that the weight of a litre of hydrogen, under the same conditions of temperature and pressure, is twice this minimum value it follows that one molecule of hydrogen must contain two atoms of hydrogen.

A consideration of the specific heats of hydrogen at constant pressure and at constant volume also leads to the conclusion that the atomicity of hydrogen is two.

It is usual to distinguish between (i) specific heat of a gas as determined at constant volume, C_v, and (ii) specific heat as determined at constant pressure, C_p, the latter being the larger of the two since more heat is absorbed by a gas which is allowed to expand and do external work, than one confined to a fixed volume.

In a monatomic gas all the heat applied goes to increase the kinetic energy of translation of the molecules; but, in a gas containing molecules of atomicities greater than one, part of the heat goes towards increasing the kinetic energy of translation, but part will also go towards increasing the kinetic energy of vibration of the atoms in the molecule.

Thus it can be shown by experiment that the ratio $\frac{C_p}{C_v}$ is less for a polyatomic gas than for a monatomic gas.

* S.T.P. (Standard Temperature and Pressure) refers to 0°C and 760 mm mercury pressure.

General values are as follows—

Atomicity of Gas	Ratio of Specific Heats, C_p/C_v
1	1·67
2	1·40 Hydrogen gives a value of 1·408
3	1·30

Molecular Weight and Vapour Density. The vapour density of a gas = weight of any volume of the gas/weight of the same volume of hydrogen, both gases being measured under the same conditions of temperature and pressure.

From Avogadro's Hypothesis it follows that—

$$\text{Vapour density} = \frac{\text{Weight of } n \text{ moles of the gas}}{\text{Weight of } n \text{ moles of hydrogen}}$$

$$= \frac{\text{Weight of 1 mole of the gas}}{\text{Weight of 1 mole of hydrogen}}$$

$$= \frac{\text{Molecular weight of the gas}}{\text{Molecular weight of hydrogen}}$$

The atomic weight of hydrogen is 1·0078, and since the atomicity of the hydrogen molecule is two, its molecular weight is 2·0156. Therefore

$$\text{Vapour density} = \frac{\text{Molecular weight of the gas}}{2{\cdot}0156} \quad . \quad (6)$$

Thus, $\text{Molecular weight} = \text{Vapour density} \times 2{\cdot}0156$

or more simply

$$\text{Molecular weight} = \text{Vapour density} \times 2 \quad . \quad . \quad . \quad (6a)$$

The Gramme Molecular Weight of any Gas at S.T.P. occupies 22·41 litres. It is an experimental fact that 1 litre of hydrogen at S.T.P. weighs 0·0897 g. Thus, taking 1 gramme molecular weight of hydrogen to be 2·0156 g, then this weight must be contained, at S.T.P., in 22·41 litres. Since vapour density = weight of 1 mole of the gas/weight of 1 mole of hydrogen and 1 gramme molecular weight of hydrogen, at S.T.P., occupies 22·41 litres, it follows that 1 gramme molecular weight of the gas, also at S.T.P., must also occupy 22·41 litres.

This volume of 22·41 litres is known as the *Gramme Molecular Volume.*

Avogadro Number. Resulting from the application of various physical methods it has been shown that the gramme molecular weight of any gas

occupying 22·41 litres at S.T.P. contains $6{\cdot}025 \times 10^{23}$ molecules. This constant is known as the Avogadro Number. Since the atomic weight of hydrogen is 1·078 the weight of an atom of hydrogen is $1{\cdot}79 \times 10^{-24}$ g.

CHEMICAL SYMBOLS

With the object of depicting the nature of chemical reactions in a form which is instantly obvious, it is usual to use symbols to represent the names of the elements involved. Thus O represents oxygen, S, sulphur, H, hydrogen, N, nitrogen and so on. These symbols however are more than a type of "short-hand" sign for the names of the elements. The symbol O, as well as being a symbol for the name oxygen, also represents one atomic weight (i.e. 16 parts by weight) of oxygen, similarly, the symbol S represents one atomic weight of sulphur (32 parts by weight). In other words, the use of the symbol of an element implies one atomic weight of the element in question.

Since the names of many elements commence with the same letter, two letters often have to be used for a chemical symbol. Thus, C represents one atomic weight of carbon, but Ca stands for one atomic weight of calcium and Cl for one atomic weight of chlorine. In addition, the chemical symbols for certain of the elements are derived from their Latin names, thus Cu represents one atomic weight of copper, Ag stands for one atomic weight of silver, Fe for one atomic weight of iron, and so on.

These symbols are international and a complete list is included in the table of atomic weights which is given on p. 50.

VALENCY (OR VALENCE)

When two elements react together, a chemical compound is formed and the name of such a compound ends with the suffix "-ide." Thus, when hydrogen and chlorine react together they form hydrogen chloride, the interaction of calcium and carbon gives rise to calcium carbide, and the chemical union of zinc and oxygen produces zinc oxide.

A consideration of the four compounds, hydrogen chloride, HCl, water, H_2O, ammonia, NH_3, and methane or marsh gas, CH_4, shows that the element hydrogen is present in each. It is also an experimental fact that one atomic weight of each of the four elements, chlorine, oxygen, nitrogen and carbon, is capable of combining with varying numbers of atomic weights of hydrogen. In actual fact, one atomic weight of chlorine combines with one atomic weight of hydrogen; one atomic weight of oxygen combines with two atomic weights of hydrogen; one atomic weight of nitrogen with three atomic weights of hydrogen; and one atomic weight of carbon with four atomic weights of hydrogen.

The number of atomic weights of hydrogen with which one atomic weight of an element will combine or displace is known as its *valency* (or *valence*).

The following are some of the elements and their valencies.

TABLE I

Valency Values for some Common Elements

I	II	III	IV	V	VI
Sodium	Calcium	Aluminium	Tin	Phosphorus	Sulphur
Potassium	Strontium	Iron	Lead		
Silver	Barium	Chromium	Carbon		
Mercury	Zinc	Nitrogen	Silicon		
Fluorine	Magnesium	Phosphorus			
Chlorine	Manganese				
Bromine	Copper				
Iodine	Iron				
	Nickel				
	Tin				
	Lead				
	Mercury				
	Oxygen				
	Sulphur				
	Carbon				

If an element exhibits a valency of one it is said to be *monovalent* (or *univalent*); if its valency is two it is said to be *divalent*. Elements with valencies of three, four, five, six, seven and eight being termed *tri-*, *tetra-*, *penta-*, *hexa-*, *hepta-* and *octa*-valent respectively.

An important use of valency is the help it affords in the writing of chemical formulae. In order to write the formula of a chemical compound it is best, until facility is obtained, to mark the symbol of the element with its valency, thus—

Na^{I} or Ca^{II} or Al^{III}

and Cl^{I} or O^{II} or N^{III}

In writing the formula for a chemical compound formed by the union of two elements the following rule must be observed: *The total number of atoms of the two elements which combine must have equal total combining capacities*, that is, identical total valencies. Thus, the formula for sodium chloride is NaCl, that of potassium fluoride, KF, and that of silver iodide, AgI, all these constituent elements being monovalent. Similarly, in the case of any pair of elements in the same valency group, the formula for calcium oxide is CaO, that of zinc sulphide, ZnS and that of aluminium phosphide, AlP.

The formulae of compounds formed by the chemical union of elements from differing valency groups is illustrated by the following examples.

(1) Aluminium oxide has the formula, Al_2O_3

Al_2^{III} has a total valency of $(2 \times 3) = 6$
O_3^{II} has a total valency of $(3 \times 2) = 6$

(2) Barium chloride has the formula, $BaCl_2$

Ba_1^{II} has a total valency of $(1 \times 2) = 2$
Cl_2^{I} has a total valency of $(2 \times 1) = 2$

The formula of a compound gives in condensed form the following information—

(i) the elements which have combined to form the compound,
(ii) the proportion by weight of each of these elements, and
(iii) the molecular weight of the compound.

Given the percentage composition of a compound, its formula may be derived as is illustrated by the following example.

The percentage composition of calcium carbonate is as follows—

Calcium	40·0
Carbon	12·0
Oxygen	48·0

In a chemical compound the percentage by weight of each element present is proportional to the number of atoms of that element per molecule of the compound, and to the atomic weight of the element in question.

Thus, for example—

$$\text{Weight of element A in compound B} = \text{Atomic weight of element A} \times \text{No. of atoms of A per molecule of B}$$

Therefore

$$\text{No. of atoms of element A in 1 molecule of compound B} = \frac{\text{Percentage of element A in compound B}}{\text{Atomic weight of element A}}$$

Thus, in the case of calcium carbonate

$$\text{No. of atoms of calcium per molecule of calcium carbonate} = \frac{\text{Percentage of calcium}}{\text{Atomic weight of calcium}} = \frac{40}{40} = 1$$

Similarly

$$\text{No. of atoms of carbon per molecule of calcium carbonate} = \frac{12}{12} = 1$$

And

$$\text{No. of atoms of oxygen per molecule of calcium carbonate} = \frac{48}{16} = 3$$

Therefore, the ratio of the atoms of calcium:carbon:oxygen are 1:1:3.
In other words, the formula of calcium carbonate is $CaCO_3$.

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Elements with more than one valency. From Table 1, it will have been noted that a number of the elements are capable of exhibiting more than one valency. This fact has already been implied in the Law of Multiple Proportions. Thus, for example, iron forms two complete series of compounds as follows—

Compounds in which Iron Exhibits a Valency of Two (Ferrous Compounds)		Compounds in which Iron Exhibits a Valency of Three (Ferric Compounds)	
Ferrous oxide	FeO	Ferric oxide	Fe_2O_3
Ferrous chloride	$FeCl_2$	Ferric chloride	$FeCl_3$
Ferrous hydroxide	$Fe(OH)_2$	Ferric hydroxide	$Fe(OH)_3$
Ferrous sulphate	$FeSO_4$	Ferric sulphate	$Fe_2(SO_4)_3$

Similarly, phosphorus forms two series of compounds in which it exhibits valencies of three and five respectively.

Compounds in which Phosphorus Exhibits a Valency of Three		Compounds in which Phosphorus Exhibits a Valency of Five	
Phosphorus trioxide	P_2O_3	Phosphorus pentoxide	P_2O_5
Phosphorus trichloride	PCl_3	Phosphorus pentachloride	PCl_5

A few compounds occur in which one element exhibits exceptional valency. For example, nitrogen normally exhibits a valency of three or five, but there are three oxides of nitrogen with the formulae, N_2O, NO, and NO_2, in which nitrogen exhibits valencies of one, two, and four respectively. These compounds, however, are single compounds and no series of compounds are formed in which nitrogen exhibits valencies of one, two, or four.

Given the formula of a chemical compound its percentage composition may be calculated. The following example illustrates the method involved.

$$\text{Percentage of element A in compound B} = \frac{\text{Atomic weight of element A} \times \text{No. of atoms of element A per molecule of B}}{\text{Molecular weight of compound B}} \times 100$$

Thus, in the case of sodium chloride (NaCl)—

$$\text{Percentage sodium} = \frac{23 \times 1 \times 100}{(23 + 35{\cdot}5)} = 39{\cdot}4$$

and

$$\text{Percentage chlorine} = \frac{35{\cdot}5 \times 1 \times 100}{(23 + 35{\cdot}5)} = 60{\cdot}6$$

Similarly, in the case of ferric oxide (Fe_2O_3)—

$$\text{Percentage iron} = \frac{56 \times 2 \times 100}{(56 \times 2) + (16 \times 3)} = 70$$

and

$$\text{Percentage oxygen} = \frac{16 \times 3 \times 100}{(56 \times 2) + (16 \times 3)} = 30$$

CHEMICAL EQUATIONS

Chemical equations are condensed statements in terms of atomic weights in which chemical symbols and formulae represent the reactions of chemical substances.

Thus, the statement

Magnesium	+	Oxygen	=	Magnesium oxide
(2 × 24·32 parts by weight)		(2 × 16 parts by weight)		(2 × 40·32 parts by weight)

may be written in the form of the following chemical equation—

$$2Mg + O_2 = 2MgO$$

In this chemical equation all the implications of the previous statement of words are conveyed with precisely the same quantitative meaning by the symbols and formulae.

Again the following statement,

Sodium chloride + Silver nitrate = Silver chloride ↓ + Sodium nitrate

may be rewritten thus—

$$NaCl + AgNO_3 = AgCl\downarrow + NaNO_3$$

The use of the arrow, thus ↓, indicates that the substance quoted immediately before this sign is precipitated as a result of the chemical reaction which the chemical equation depicts. Similarly, an arrow used thus ↑, indicates the evolution of a substance as a gas.

A group of atoms which acts as a group or unit in a chemical reaction is known as a *radical*. Thus, in the case of silver nitrate, $AgNO_3$, the group "NO_3" is known as the nitrate radical, and in ammonium chloride, NH_4Cl, the group "NH_4" is termed the ammonium radical.

The number placed in front of a symbol or formula of a substance indicates the number of molecules of that substance which react, whilst the number placed as a subscript after the symbol of an element indicates the number of atoms of that element in a molecule. Thus, the symbol O_2 indicates one molecule of oxygen containing two atoms of oxygen, whilst $2Fe_2O_3$ indicates two molecules of ferric oxide, each molecule containing two atoms of iron and three atoms of oxygen.

The Writing of Chemical Equations. Three stages are involved in the writing of chemical equations, namely—

(*a*) The names and molecular formulae of the reactants, and of the products, are ascertained.

(*b*) The molecular formulae of reactants and products are written down in skeleton form, with the formulae for the reactants on the left and the products on the right.

(*c*) The skeleton equation is balanced (or adjusted).

These steps may be traced in the following example—

(i) Iron and oxygen combine to form ferric oxide, and the molecular formulae for these substances are Fe, O_2 and Fe_2O_3.

(ii) The skeleton equation for the reaction involved is

$$Fe + O_2 = Fe_2O_3$$

(iii) This skeleton equation is then balanced as follows; working back from the largest formula (i.e. Fe_2O_3), it is clear that the only way to obtain oxygen atoms in threes is to take six oxygen atoms (i.e. $3O_2$). This gives two molecules of ferric oxide (i.e. $2Fe_2O_3$). In turn, this requires four atoms of iron (i.e. 4Fe). Therefore, the balanced equation is

$$4Fe + 3O_2 = 2Fe_2O_3$$

Calculations Involving Chemical Equations. Equations are invaluable as a means of calculating the weight of a product obtained from given weights of reactants or, alternatively, the amount of materials necessary to obtain a certain weight of product.

Thus, for example, it may be required to calculate what weight of hydrogen is produced by the action of sulphuric acid upon 28 lb of zinc. In such a calculation the following steps should be followed.

(*a*) Write down the chemical equation representing the reaction involved, in this specific case—

$$Zn + H_2SO_4 = H_2 + ZnSO_4$$

(*b*) Write in underneath each formula or symbol the reacting weights involved, thus—

$$\underset{(65{\cdot}4)}{Zn} + H_2SO_4 = \underset{(2)}{H_2} + ZnSO_4$$

Notes: Atomic weight of zinc is 65·4.

Atomic weight of hydrogen is 1 (in round figures), and since one molecule of hydrogen is evolved (i.e. two atoms), the molecular weight of hydrogen is required in this calculation, that is, 2.

(*c*) State the reacting weights of the substances as follows—

65·4 parts by weight of zinc acted upon by sulphuric acid evolve 2 parts by weight of hydrogen.

Therefore,

65·4 lb of zinc acted upon by sulphuric acid evolve 2 lb of hydrogen.

So that,

28 lb of zinc acted upon by sulphuric acid would evolve $\frac{2 \times 28}{65{\cdot}4}$ lb of hydrogen = 0·858 lb of hydrogen.

Note: The reacting weight of sulphuric acid is not introduced into the calculation.

EQUIVALENT WEIGHTS

All the elements except the inert gases are capable of entering into chemical combination with one another. In the formation of chemical compounds the elements are only capable of reaction together in certain definite proportions. For the purpose of evaluating these combining weights it is usual to determine the weight of an element which will combine with or displace a standard weight of a standard element. The standard element employed is oxygen, and the standard weight is 8 g of oxygen.

Thus, 1·0078 g of hydrogen will combine with 8 g of oxygen and 1·0078 is known as the *equivalent weight* of hydrogen. Similarly, since 35·46 g of chlorine will combine with 1·0078 g of hydrogen, 35·46 g must be the equivalent weight of chlorine. Similarly since 107·88 g of silver will combine with 35·46 g of chlorine to form silver chloride, the equivalent weight of silver is 107·88.

When equivalent weights are reported in grammes it is usual to refer to them as *gramme equivalent weights.*

Although each element may possess only *one* atomic weight, most elements exhibit more than one valency. And since

$$\text{Equivalent weight} \times \text{Valency} = \text{Atomic weight}$$

it follows that all elements exhibiting more than one valency will likewise possess more than one equivalent weight.

Determination of Equivalent Weights

It will be appreciated that the determination of equivalent weights is of fundamental importance both by virtue of their practical application to quantitative operations, such as chemical analysis, and also as a basis for the determination of atomic weights.

A number of methods are available for the determination of equivalent weights and they may be classified as shown below.

(1) Hydrogen displacement from an acid or an alkali
(2) Oxide methods
(3) Chloride method

(4) Chemical replacement method
(5) Electrolytic method
(6) Conversion method
(7) Formation of the hydride
(8) Titration method

Hydrogen Displacement from an Acid or an Alkali. This method is especially suitable for such metals as magnesium, zinc and aluminium, which will act upon acids and alkalis giving rise to the evolution of

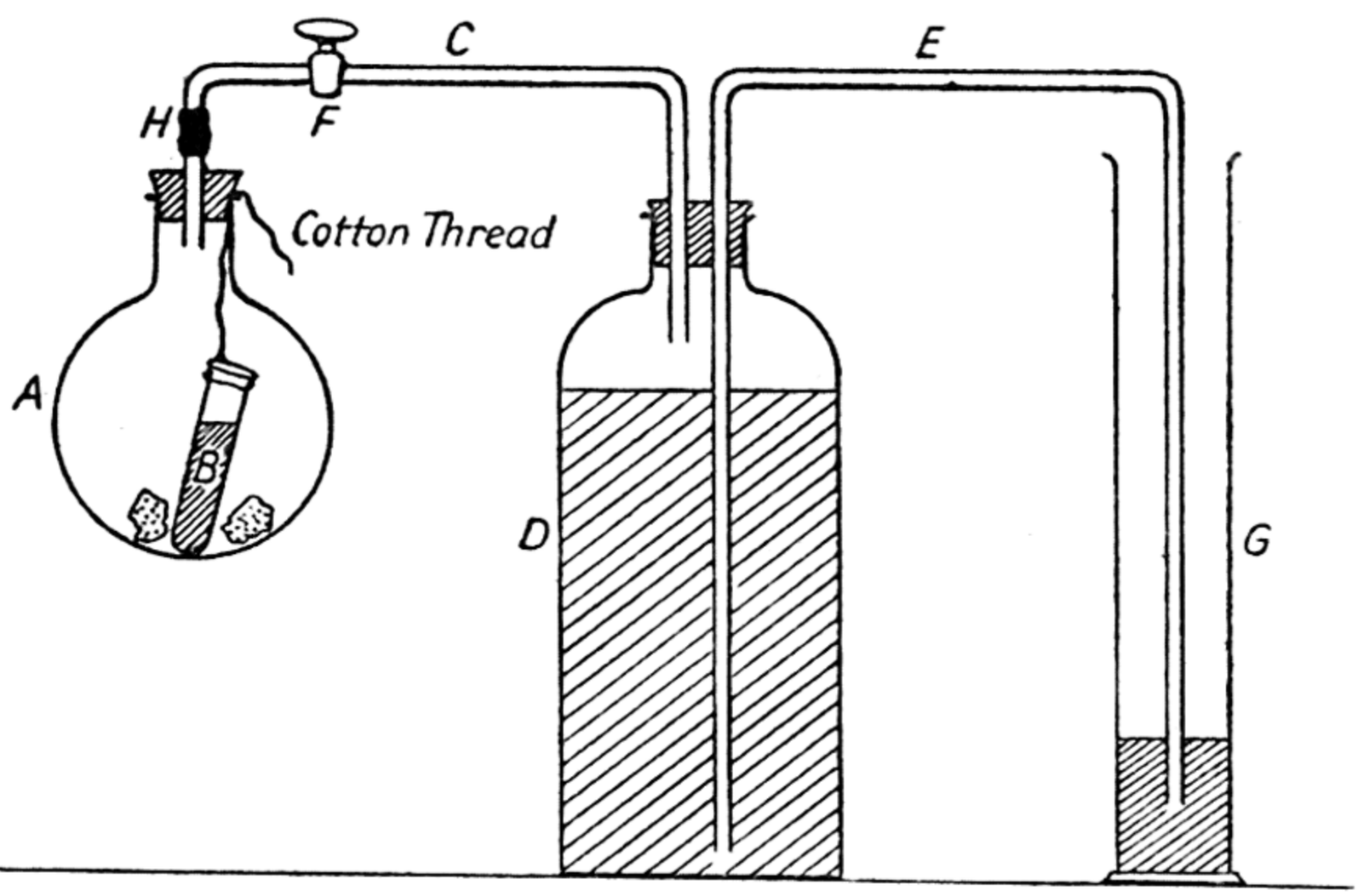

FIG. 3. Determination of Equivalent Weight by Displacement of Hydrogen from an Acid or an Alkali

hydrogen. The following chemical equations represent the reactions which occur.

$$Mg + 2HCl = MgCl_2 + H_2$$
$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
$$Zn + 2NaOH = Na_2ZnO_2 + H_2$$
$$2Al + 6NaOH = 2Na_3AlO_3 + 3H_2$$

The general principle of this method is that a known weight of the metal whose equivalent weight is required is allowed to act upon an excess of a selected acid or alkali, the hydrogen evolved being collected and its volume measured. Knowing the volume of the hydrogen under specific atmospheric conditions, the weight of the hydrogen is then calculated, this latter figure in conjunction with the known weight of the metal permitting the evaluation of the equivalent weight of the metal.

A suitable apparatus for carrying out this determination is shown in Fig. 3. In the first instance, the known weight of metal is contained within the reaction flask, *A*, the excess of acid or of alkali being contained in the test tube, *B*. The reaction flask is connected by means of a delivery tube,

C, to the storage bottle, *D*, which is filled with water. Another delivery tube, *E*, permits of water to be driven from the storage bottle into the graduated cylinder, *G*. For the purpose of operation the known weight of the metal is placed in the reaction flask and an excess of acid (or of alkali) poured into the test tube which is maintained in the upright position by means of a cotton thread, which is clamped between the neck of the flask and the rubber bung. The tap, *F*, is opened and gentle suction applied to the open end of the delivery tube, *E*. A small volume of water flows out of the tube, but if the apparatus is air-tight this flow should quickly cease. The graduated cylinder, *G*, is then placed into position, the reaction flask tilted to permit of the the mixing of the metal and acid (or alkali), the flexible rubber connecting tube, *H*, making this movement possible. Hydrogen is liberated which passes along the delivery tube, *C*, and displaces water from the storage bottle into the graduated cylinder in which it can be measured. This volume of water expelled from the storage bottle represents the volume of hydrogen evolved in the reaction flask. The method of calculation of the equivalent weight from data obtained as described above will be apparent from the following numerical example.

Weight of metal = 0·03 g

Volume of moist hydrogen measured at 12°C and 750·5 mm pressure = 30·5 ml

Pressure of water vapour at 12°C = 10·5 mm

Therefore, volume of *dry* hydrogen at S.T.P. $= \frac{30{\cdot}5 \times (750{\cdot}5 - 10{\cdot}5) \times 273}{760 \times (273 + 12)}$ ml

$= 28{\cdot}5$ ml

Now, 1 litre of hydrogen at S.T.P. weighs = 0·09 g

Therefore, weight of 28·5 ml of hydrogen = 0·00009 × 28·5 g

Thus, equivalent weight of the metal $= \frac{0{\cdot}03 \times 1{\cdot}008}{0{\cdot}00009 \times 28{\cdot}5}$

$= \underline{\underline{11{\cdot}79}}$

Oxide Methods. Three oxide methods are available for the determination of equivalent weight; they are respectively—

(*a*) Direct chemical combination of the element and oxygen, to form the oxide of the element;

(*b*) Indirect formation of the oxide via an intermediate compound such as a nitrate; and

(*c*) Reduction of an oxide to the element.

These three methods will be discussed in the order named.

Direct Synthesis of Oxide. The principle of this method will be illustrated by reference to the element carbon.

If a known weight of carbon is burnt in an excess of pure, dry oxygen it will form the gaseous oxide, carbon dioxide, CO_2. This oxide may be weighed by absorption in a reagent such as potassium hydroxide solution contained within a suitable vessel, the vessel being weighed before and after absorption. A suitable apparatus for this determination is shown in Fig. 4. Pure dried oxygen is allowed to enter, through the leading tube, *L*, into the combustion tube, *A*, a known weight of carbon being contained on the combustion boat, *B*. The remaining part of the combustion tube contains granulated cupric oxide. This cupric oxide is for the purpose of oxidizing traces of carbon monoxide which may be formed along with carbon dioxide. The whole length of the combustion tube and its contents are heated. The exit gases consisting of carbon dioxide and excess oxygen

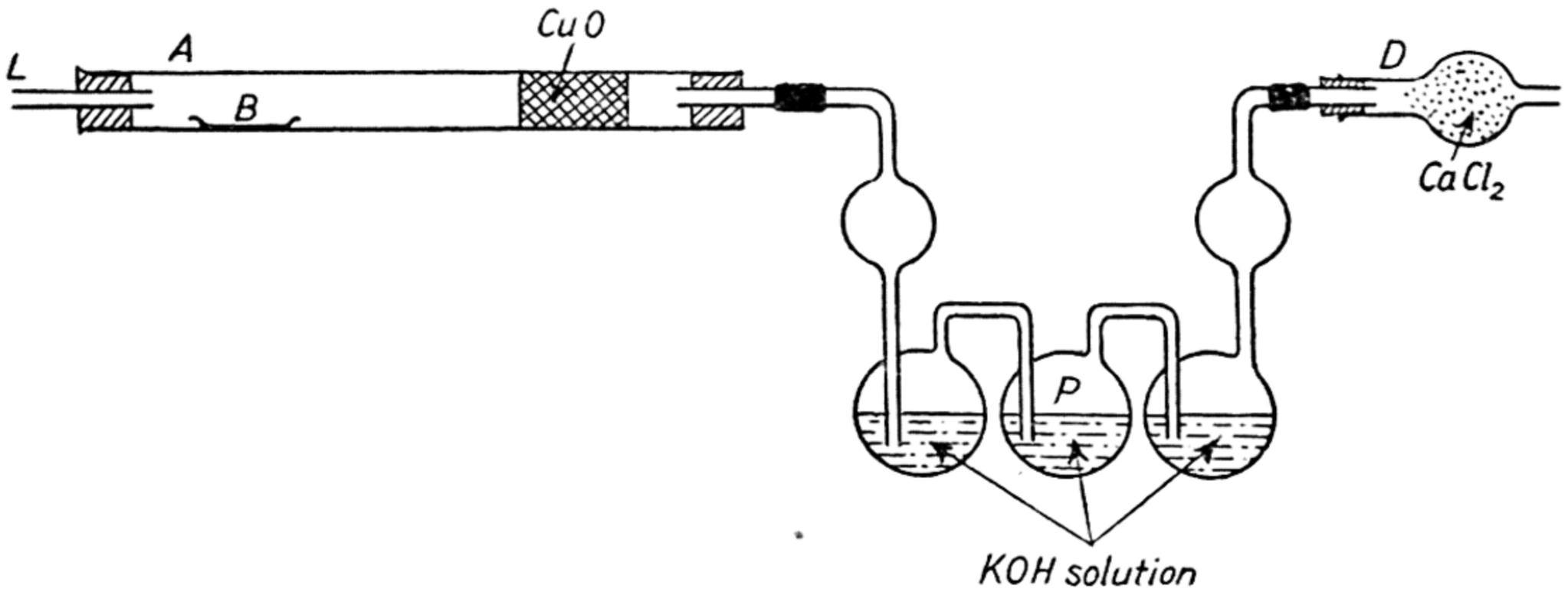

FIG. 4. Determination of Equivalent Weight by Direct Synthesis of Oxides

pass from the combustion tube into the potash bulbs, *P*, containing potassium hydroxide solution. These bulbs are capable of being disconnected from the apparatus for the purpose of weighing, and they are weighed before and after combustion of the carbon has occurred. A safety trap to prevent the entrance of moisture and carbon dioxide from the air into the potash bulbs takes the form of a calcium chloride drying tube, *D*.

From the known weight of carbon oxidized and the experimentally determined weight of carbon dioxide, the equivalent weight is then calculated.

Indirect Synthesis of Oxide via an Intermediate Compound. This method is especially useful for metals like magnesium or zinc which form readily volatile oxides on direct union with oxygen, or for metals like copper, tin and lead which only form oxides at a slow rate on direct union with oxygen.

The most common intermediate compound is the nitrate. All the metals quoted above, except tin, will readily form nitrates, when acted upon by nitric acid; tin forms a stannic acid. On heating, all these compounds break down, giving rise to the corresponding oxides. It is thus a simple matter to take a known weight of the metal concerned, act upon it

with an excess of nitric acid and then evaporate the solution thus formed to dryness, and finally heat the metal nitrate (or stannic acid in the case of tin) to red heat until a constant weight is obtained. This final weight, that is the weight of the metal oxide, thus permits, in conjunction with the known initial weight of metal, of the evaluation of the equivalent weight of the metal.

Reduction of an Oxide to the Element. This modification is particularly suitable for those oxides which are easily reduced by the chemical action of hydrogen or of carbon monoxide, or of coal gas.

A suitable apparatus for this determination is shown in Fig. 5. A known weight of the metal oxide is contained within the combustion boat, *A*, the

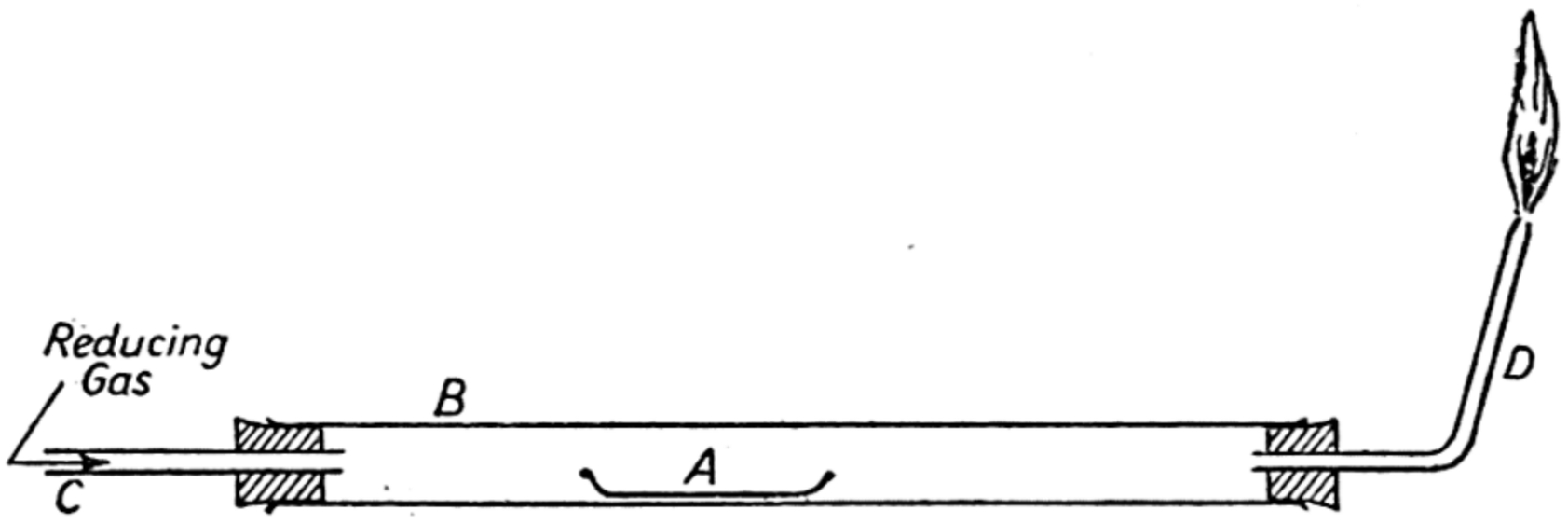

FIG. 5. Determination of Equivalent Weight by Reduction of an Oxide to the Element

boat and its contents being contained within the combustion tube, *B*. The combustion tube and its contents are heated to red heat. A reducing gas (e.g. hydrogen, carbon monoxide or coal gas) is allowed to enter the combustion tube via the leading tube, *C*. An excess of the reducing gas is employed, the excess being burnt at the end of the delivery tube, *D*. The reducing gas passing over the heated metal oxide reduces it to the metal. The reducing gas is passed until the contents of the combustion boat attain a constancy of weight thus indicating that reduction is complete. Then, knowing the original weight of the metal oxide and the experimentally determined weight of the metal, the equivalent weight of the metal may be calculated.

The following data will make clear the method of calculation.

Experimental Determination of the Equivalent Weight of Copper

Weight of cupric oxide, CuO	=	1·000 g
Weight of copper produced by reduction	=	0·799 g
Weight of oxygen combined with 0·799 g of copper	=	1·000—0·799 g
	=	0·201 g
Therefore, gramme equivalent weight of copper	=	$\frac{0{\cdot}799 \times 8}{0{\cdot}201}$ g
	=	31·8 g

Chloride Method. This method is particularly suitable for those elements which form soluble chlorides. The method depends for its success upon the fact that silver chloride is practically insoluble in water, and that silver may, without undue difficulty, be obtained in a high degree of purity.

The principle involved in this method will be exemplified by means of the following example. Suppose it is desired to determine the equivalent weight of the element, X, which forms a chloride readily soluble in water.

A small quantity of the pure chloride is weighed out, dissolved in a minimum quantity of distilled water and the solution acidified with a little nitric acid. Silver nitrate solution is then added until no further precipitation occurs. The precipitated silver chloride is then filtered, washed, dried and weighed.

The chemical reaction which occurs on addition of the silver nitrate is as follows—

$$XCl + AgNO_3 = AgCl\downarrow + XNO_3$$

The equivalent weight of the chloride, XCl is that weight of this compound which will produce 143·34 g of silver chloride. This weight is the sum of the equivalent weights of silver and chlorine respectively (i.e. 107·88 + 35·46). Since the equivalent weight of the chloride XCl is the sum of the equivalent weights of the element X and chlorine respectively, then the equivalent weight of X may be obtained by subtracting 35·46 from the equivalent weight of XCl.

In the case of certain elements it has been found preferable to precipitate silver bromide instead of the silver chloride. The former compound like the latter is well known for its exceedingly low solubility in water.

Chemical Replacement Method. This method depends upon the fact that certain metals (e.g. zinc) will displace other metals (e.g. copper) from aqueous solutions of their salts.

Thus, for example, the addition of metallic zinc to an aqueous solution of cupric sulphate gives rise to the precipitation of metallic copper and the formation of zinc sulphate which remains in solution. The reaction involved is as follows—

$$CuSO_4 + Zn = Cu\downarrow + ZnSO_4$$

The method thus involves the use of a known weight of metallic zinc which is added to the aqueous solution of the salt of the metal whose equivalent weight it is required to determine. The metal is thrown out of the solution as a precipitate which is filtered, washed, dried and then finally weighed. The method of calculation will be clear from the following example in which the equivalent weight of copper is determined.

Numerical Example

Weight of zinc foil = 1·00 g

Weight of copper precipitated = 0·97 g

Given that the equivalent weight of zinc = 32·7

Therefore, the equivalent weight of copper $= \frac{0{\cdot}97 \times 32{\cdot}7}{1{\cdot}00}$

$= 31{\cdot}8$

Electrolytic Method. This method involves the application of Faraday's Law of Electrolysis.

Faraday discovered that the same quantity of electricity passing through solutions of different electrolytes* liberates weights of elements proportional to their equivalent weights. Thus, the quantity of electricity which leads to the liberation of 1·0078 g of hydrogen from dilute sulphuric acid will also liberate 8 g of oxygen, or 31·8 g of copper, or 107·88 g of silver, or 65·7 g of gold from their respective compounds. These weights are the equivalent weights for the elements quoted.

Therefore, knowing the weight of one element liberated by electrolysis and its equivalent weight, the equivalent weight of another element liberated in the same time and in the same circuit may be calculated.

Conversion Method. This method involves the quantitative conversion of one compound into another. Thus, by repeated treatment of potassium chloride, KCl, with nitric acid, HNO_3, the compound, potassium nitrate, KNO_3, may be formed. The chemical reaction involved is represented by the following equation—

$$KCl + HNO_3 = KNO_3 + HCl$$

This method may be used, for example, to determine the equivalent weight of nitrogen.

Since the equivalent weights of potassium, chlorine and oxygen are all known with a considerable degree of precision, then

$$\frac{\text{Weight of potassium chloride}}{\text{Weight of potassium nitrate}} = \frac{\text{Equivalent weight of potassium chloride}}{\text{Equivalent weight of potassium nitrate}}$$

Thus, the equivalent weight of potassium nitrate may be evaluated, and since this is equal to the sum of the equivalent weights of potassium, nitrogen and oxygen respectively, and since those for potassium and oxygen are known, then it becomes a simple matter of arithmetic to evaluate the equivalent weight of nitrogen.

* The term *electrolyte* will be discussed more fully later (*see* p. 238).

Formation of the Hydride. This method is similar to the other methods described and finds greatest application in connexion with the non-metallic elements.

Titration Method. All acids contain replaceable hydrogen, that is, hydrogen which may be replaced by a metal.

This method involves the employment of a known excess of an acid to which is added a known weight of the metal whose equivalent weight is desired. The metal dissolves in the acid, liberating hydrogen in the process and also forming the metallic salt which remains in solution. The excess of the acid is determined by addition of a solution of an alkali of known concentration until the whole of the residual acid has been neutralized, the production of the neutral condition being made evident by means of a colour change of a suitable compound termed an *indicator*. Knowing the concentration of the alkali used, and the volume required to effect neutralization, and also knowing the concentration of the acid and initial volume, and the weight of the metal dissolved, it is possible to evaluate that volume of the acid required to dissolve the metal. The weight of hydrogen in this volume of acid may then be easily calculated and the equivalent weight of the metal evaluated.

CHAPTER 2

THE DETERMINATION OF MOLECULAR AND ATOMIC WEIGHTS

FROM a knowledge of the laws governing the manner in which the elements combine together, both on the weight basis as well as on the volume basis, it is possible to pass on to the determination of molecular and atomic weights.

DETERMINATION OF MOLECULAR WEIGHTS

Methods for the determination of the molecular weight of a substance may be classified as follows—

(*a*) Methods in which the molecular weight is calculated from determinations of the density of the vapour of the substance.

(*b*) Methods in which the molecular weight is calculated from determinations of such properties as osmotic pressure, vapour pressure, freezing point and boiling point of a solution of the substance under investigation in a suitable solvent.

It is important to appreciate at the outset that the numerical value of the molecular weight of the substance as determined independently by both methods will not necessarily be the same. This is due to the fact that the molecules of the substance may undergo dissociation into simpler compounds or into atoms having lower molecular weights, or alternatively association into double or more complex molecules of higher molecular weight.

It will be more convenient here to discuss only those methods of molecular weight determination which involve measurements of vapour density, the consideration of the determination of molecular weights in solution being deferred until later, when solutions and their properties are discussed in detail in Chapter 8.

Determination of Molecular Weight from Measurements of Vapour Density

The atomic and molecular weights of a volatile solid or liquid element or compound may be calculated from the density of its vapour. The vapour density of a volatile substance is the weight of a given volume of vapour compared with the weight of an equal volume of hydrogen measured under the same conditions of temperature and pressure.

Three general methods are available for the determination of the density of a vapour; they are Dumas' method, Victor Meyer's method and

Hofmann's method respectively. In Dumas' method the weight of a known volume of the vapour of the substance at known temperature and pressure is determined, whilst in Victor Meyer's method and in Hofmann's method a determination is made of the volume at known temperature and pressure of a given weight of the vapour of the substance.

It should be noted that, owing to the experimental difficulties which obtain when employing these methods, it is only possible to obtain an approximate value for the molecular weight; nevertheless, these results are most valuable since they may be employed to evaluate the exact molecular weight of a volatile substance.

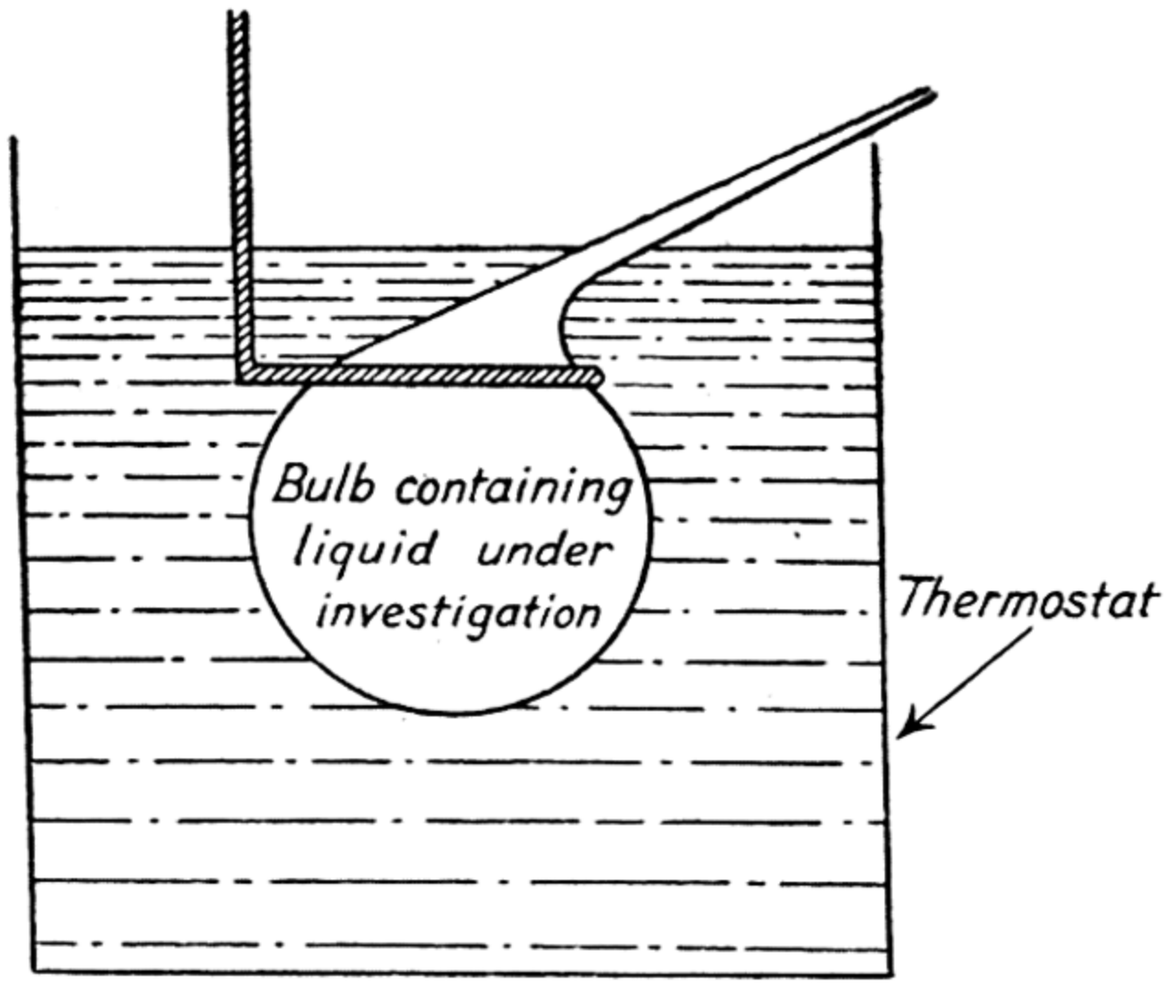

FIG. 6. Dumas' Method for the Determination of Vapour Density

Dumas' Method. This method permits of a fair degree of accuracy but necessitates the use of a comparatively large volume of the substance under investigation.

About 10 ml of the liquid under investigation is drawn into a thin-walled glass bulb, of about 150 ml capacity, by warming the bulb slightly and then allowing it to cool with the tip of the capillary tube placed below the surface of the liquid under investigation. The bulb and its contents are then fixed in place in a thermostat at a temperature sufficiently high to cause the liquid under investigation to boil (*see* Fig. 6). The vaporizing of the liquid causes the air originally in the bulb to be expelled. As soon as the vapour ceases to stream from the capillary, the tip of the capillary is sealed off, and the bulb cooled and then weighed. The tip of the capillary is broken off under water which enters until the bulb is completely full. The bulb is then weighed full of water along with the piece of the tip broken off. The method of calculation will be evident from the example shown on p. 28.

Determination of the Molecular Weight of Carbon Disulphide

Weight of water contained in Dumas' bulb = 104 g

Therefore, volume of bulb = 0·104 litres

Weight of carbon disulphide = 0·26 g

Therefore, under the experimental conditions prevailing, 0·104 litre of carbon disulphide weighs = 0·26 g

And under the same experimental conditions 22·4 litres of carbon disulphide (i.e. the gramme molecular volume) weigh

$$= \frac{0{\cdot}26 \times 22{\cdot}4}{0{\cdot}104} \text{ g}$$

$$= \underline{\underline{76{\cdot}2 \text{ g}}}$$

This result gives the order of magnitude of the molecular weight of carbon disulphide so that on introducing atomic weights into the empirical formula, CS_2 for carbon disulphide, the exact molecular weight of 76 may be evaluated.

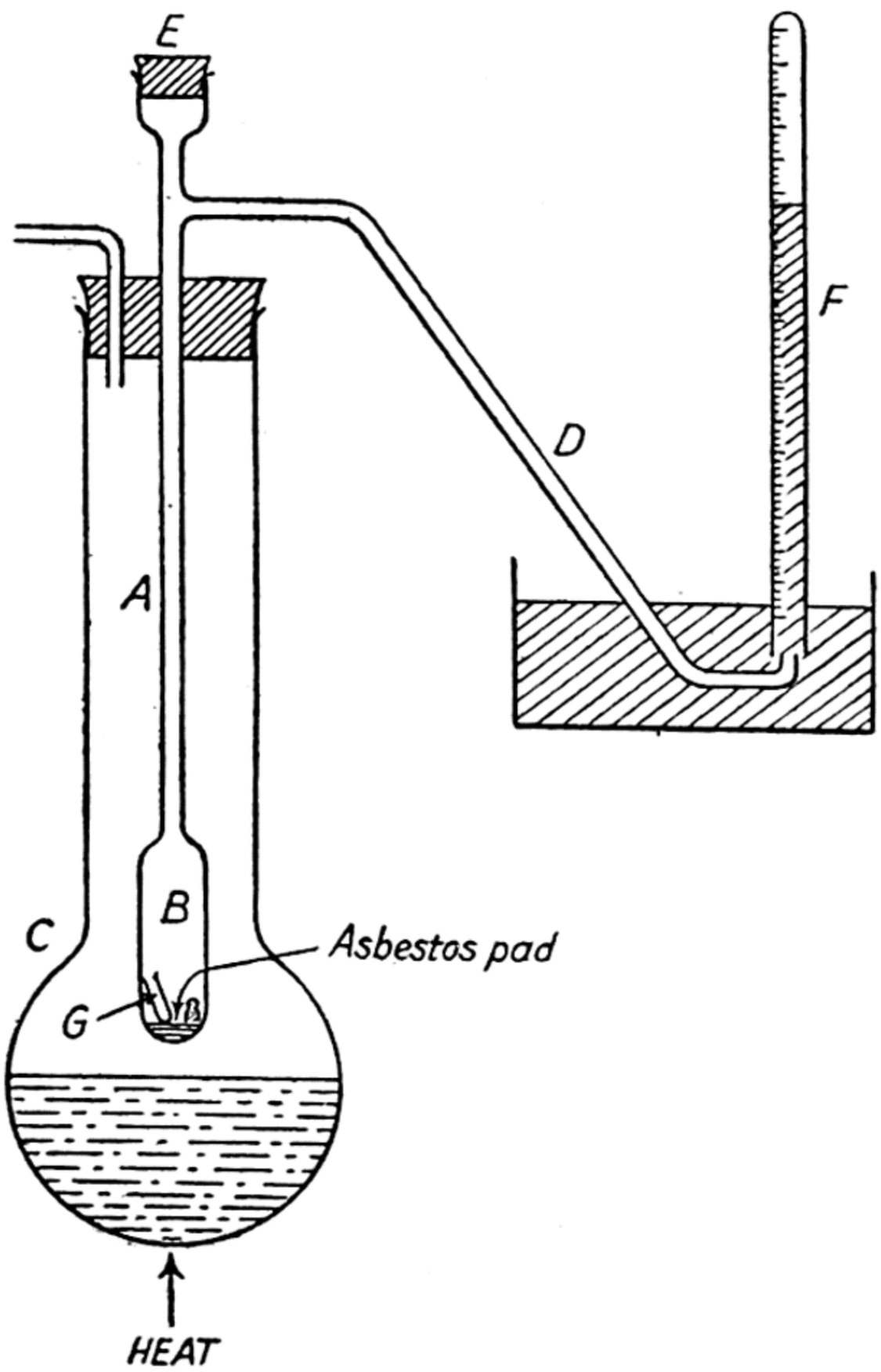

FIG. 7. Victor Meyer's Method for the Determination of Vapour Density

Victor Meyer's Method. This method, although less accurate than Dumas' method, has the advantage that it is very rapid. If it is merely a question of deciding the relationship existing between empirical and molecular formulae, this method is usually sufficiently accurate.

A measurement is made of the volume of air displaced by the vaporization of a known weight of volatile liquid or solid. The apparatus consists essentially of a long glass tube, *A*, having a bulb, *B*, blown on one end (*see* Fig. 7). The substance under investigation is contained within a small glass bottle which is dropped down the long glass tube which fits into an outer jacket, *C*, containing water or some other liquid having a boiling point above the boiling point of the liquid under investigation.

The liquid in the outer jacket is raised to boiling point, the attainment of a steady temperature being indicated by the cessation of air bubbles issuing from the side tube, *D* (the stopper, *E*, being meanwhile inserted

in the top of the long glass tube). The graduated measuring cylinder, *F*, is then filled with water, inverted and placed over the open end of the side tube; the small glass bottle, *G*, containing a known weight of substance is dropped down the long glass tube, *A* (the stopper, *E*, being momentarily removed for this purpose). The fall of the small glass bottle is broken by a pad of asbestos placed at the bottom of the long glass tube. The liquid in the bottle being raised to a temperature above its boiling point immediately vaporizes, blows off the small stopper and the vapour fills the lower portion of the bulb, expelling air in the process. The air thus displaced is collected in the graduated tube, *F*. When no more bubbles of air issue from the side tube the volume of air is measured and the temperature and pressure of the room noted. The volume of air actually measured is the volume the vapour would have occupied at the room temperature and pressure. The following example illustrates the method of calculation.

Determination of the Molecular Weight of Chloroform

Weight of chloroform taken = 0·1 g

Volume of expelled moist air measured at 15°C and 773 mm = 20·0 ml

Vapour pressure of water at 15°C = 13 mm

Therefore, volume of dry air at S.T.P. $= \frac{20 \times 273 \times (773 - 13)}{288 \times 760}$ ml

$= 18{\cdot}95$ ml

This is also the volume occupied by the chloroform vapour.

Then, weight of 18·95 ml chloroform under the experimental conditions obtaining = 0·1 g

Therefore, weight of 22·4 litres of chloroform (i.e. the gramme molecular volume) under the same experimental conditions $= \frac{0{\cdot}1 \times 22{\cdot}4 \times 1000}{18{\cdot}95}$ g

$= \underline{\underline{118{\cdot}1 \text{ g}}}$

This result gives the order of magnitude of the molecular weight of chloroform, so that on substituting atomic weights in the empirical formula, $CHCl_3$, the exact molecular weight of 119·5 is obtained.

Hofmann's Method. In Hofmann's method a known weight of volatile liquid contained within a small stoppered tube (which the liquid must fill completely), is introduced into the vacuum above the mercury column in a barometer (*see* Fig. 8).

The barometer tube, *A*, is enclosed within a vapour jacket, *B*, through which steam circulates. The vapour is circulated through the jacket until conditions are stable when the specimen tube, *C*, containing a known

weight of liquid is introduced into the open end of the barometer tube below the mercury surface. The tube and its contents float up the barometer tube to the surface of the mercury where the internal pressure of the vapour established by the elevated temperature is sufficient to expel the stopper and the vapour of the liquid fills the space above the mercury. The barometer tube is graduated so that when the mercury level is stationary the volume of the vapour and its temperature and pressure can be read off. The method of calculation is similar to that employed in the previous two numerical examples.

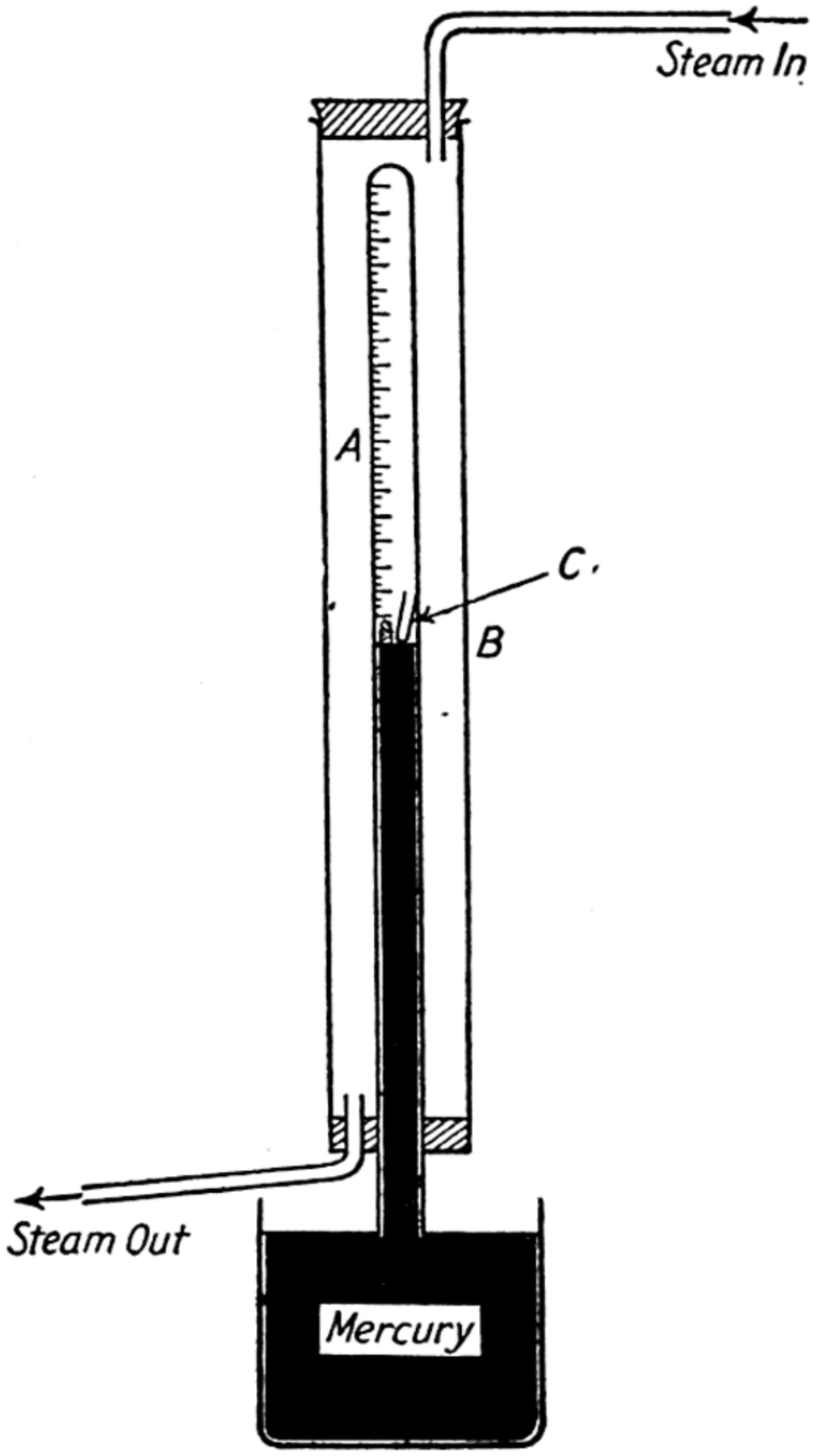

FIG. 8. Hofmann's Method for the Determination of Vapour Density

Abnormal Vapour Densities. In general, the values for molecular weights derived from measurements of vapour densities are in agreement with the values obtained from other considerations. This of course implies that the chemical constitution of the vapour is the same as that of the solid, or of the liquid from which it was derived. This assumption, however, is not always valid.

For example, the compound ammonium chloride, which has the formula NH_4Cl, has the molecular weight of 53·46 from which, following the implications of Avogadro's Hypothesis, the vapour density would be expected to be 53·46/2, that is 26·73. In actual fact, however, the vapour density is found to be 13·36 (which, it should be noted, is half 26·73).

Experiment has shown that ammonium chloride undergoes breakdown on heating according to the following reaction.

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

When the vapour of ammonium chloride is cooled, the products of the breakdown (i.e. ammonia and hydrogen chloride) recombine to form ammonium chloride. This type of reaction, reversible in nature, brought about by heating (or cooling) a substance, is known as *thermal dissociation*. If as a result of thermal dissociation each molecule of ammonium chloride gives rise to the production of equal numbers of molecules of ammonia

and hydrogen chloride, then there will be produced equal volumes of ammonia and hydrogen chloride, and the mixture of these two gases will have a density half way between the densities of ammonia and hydrogen chloride, 8·5 and 18·23 respectively, that is, (8·5 + 18·23)/2 = 13·36. This particular reaction, therefore may be depicted as follows—

$$NH_4Cl \underset{\text{Fall in temperature}}{\overset{\text{Rise in temperature}}{\rightleftharpoons}} NH_3 + HCl$$

Ammonium chloride is not unique since there are many substances which undergo thermal dissociation; for example, nitrogen tetroxide, N_2O_4, undergoes dissociation into nitrogen peroxide, NO_2, on heating which, in turn, at still higher temperatures, dissociates into nitric oxide, NO, and oxygen as follows—

$$\underset{\substack{\text{yellow liquid}\\ \text{at 20°C}}}{N_2O_4} \rightleftharpoons \underset{\substack{\text{dark brown gas}\\ \text{at 40°C}}}{2NO_2} \rightleftharpoons \underset{\text{colourless gases}}{2NO + O_2}$$

Similarly, phosphorus pentachloride, PCl_5, undergoes thermal dissociation on heating, thus—

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Also, hydrogen iodide dissociates in a similar manner—

$$2HI \rightleftharpoons H_2 + I_2$$

It is important to observe that thermal dissociation differs from thermal decomposition in that the former is reversible in nature, whilst the latter is irreversible.

Degree of Thermal Dissociation and its Evaluation. In many cases thermal dissociation is not complete and a state of equilibrium is established in which the proportion of each substance present is dependent upon the temperature and upon the pressure.

Should a substance undergo *partial thermal dissociation*, it is possible to calculate the extent or degree of dissociation from data obtained from an experimental determination of vapour density.*

The degree of thermal dissociation is defined as the fraction of one molecule of the original substance which has undergone dissociation. The *degree of dissociation* is often designated by the symbol, α. The method of calculation will be made evident by the following examples.

Example 1. Thermal Dissociation of Nitrogen Tetroxide

Let n molecules of nitrogen tetroxide be heated at constant pressure, and let the fraction of each molecule dissociated be α. Then, when equilibrium is

* This calculation is possible only provided that the dissociation involves a change in the number of molecules in the system. The full implications of this statement will be discussed more fully later (*see* p. 225).

attained there will be $n(1 - \alpha)$ molecules of nitrogen tetroxide, and $2n\alpha$ molecules of nitrogen peroxide, thus—

$$\begin{array}{c} N_2O_4 \rightleftharpoons 2NO_2 \\ n(1-\alpha) \quad 2n\alpha \end{array}$$

This equation may be reduced to its lowest terms as follows—

$$\begin{array}{c} N_2O_4 \rightleftharpoons 2NO_2 \\ (1-\alpha) \quad 2\alpha \end{array}$$

Thus, the total number of molecules present in the equilibrium mixture is $(1 - \alpha) + 2\alpha = 1 + \alpha$.

Since the pressure is maintained constant the volume will increase in the ratio of $1/(1 + \alpha)$, or conversely, the vapour density will decrease in the ratio of $1/(1 + \alpha)$. In other words, if d represents the density of the equilibrium mixture, and D the vapour density of nitrogen tetroxide, then—

$$d = \frac{D}{1+\alpha} \text{ and } \alpha = \frac{D-d}{d}$$

Example 2. Thermal Dissociation of Nickel Carbonyl

On heating, nickel carbonyl, $Ni(CO)_4$, undergoes thermal dissociation according to the following equation—

$$Ni(CO)_4 \rightleftharpoons Ni + 4CO$$

Employing the same procedure as in the case of *Example* 1, assuming that initially there are n molecules of nickel carbonyl and that the fraction of each molecule undergoing dissociation is α, then in the equilibrium mixture there will be $n(1 - \alpha)$ molecules of nickel carbonyl and $4n\alpha$ molecules of carbon monoxide. Since the nickel is precipitated as a solid, its volume may be neglected in this calculation. The equilibrium condition may be represented thus—

$$\begin{array}{c} Ni(CO)_4 \rightleftharpoons Ni + 4CO \\ n(1-\alpha) \qquad\quad 4n\alpha \end{array}$$

Reduced to its lowest terms this equation becomes—

$$\begin{array}{c} Ni(CO)_4 \rightleftharpoons Ni + 4CO \\ (1-\alpha) \qquad\quad 4\alpha \end{array}$$

Thus, the total number of molecules present in the equilibrium mixture is—

$$(1 - \alpha) + 4\alpha = 1 + 3\alpha$$

Resulting from the thermal dissociation, the vapour density will decrease in the ratio of $1/(1 + 3\alpha)$.

In other words, if d represents the density of the equilibrium mixture, and the vapour density of nickel carbonyl is 85·35, then—

$$d = \frac{85{\cdot}35}{1+3\alpha}$$

and

$$\alpha = \frac{85{\cdot}35 - d}{3d}$$

In general, therefore, if x is the number of volatile molecules produced by the thermal dissociation of one molecule of the original substance, then—

$$\text{Degree of Dissociation} = \frac{\text{Vapour density of original substance} - \text{Vapour density of equilibrium mixture}}{(x-1) \times \text{Vapour density of equilibrium mixture}}$$

DETERMINATION OF ATOMIC WEIGHTS

The accurate determination of the numerical value of the atomic weight of an element is dependent in the first instance on a knowledge either of the molecular weight, or of the equivalent weight of the element. Once either of these values is known, the determination of the correct sub-multiple in the case of the molecular weight, or the correct multiple in the case of the equivalent weight, is the only data required in order to evaluate the atomic weight of the element.

Determination of Atomic Weight when the Molecular Weight is known

By the Application of Avogadro's Hypothesis. The approximate atomic weight of a gaseous element may be determined from vapour density measurements in conjunction with a knowledge of the atomicity of the gas. The atomicity of a gaseous element may be found by a consideration of suitable volume relationships which occur when the element in question combines with other elements. This method was discussed earlier on p. 10 when dealing with the implications of Avogadro's Hypothesis.

Another method of determining the atomicity of a gaseous element involves the determination of the ratio of the specific heat of the gas at constant pressure to the specific heat at constant volume. This ratio, C_p/C_v, or γ, varies according to the atomicity of the gas under examination. Although for an ideal gas the value of γ should be constant, for real gases, other than monatomic gases, the ratio varies considerably with variation of temperature and pressure. Nevertheless, for ordinary temperatures and pressures approximate working values are as follows.

Atomicity of Gas	Value of γ
Monatomic gases . . .	1·67
Diatomic gases. . . .	1·40
Simple polyatomic gases . .	1·30

Since the direct measurement of the specific heat of a gas presents considerable difficulties, the numerical value of γ is usually determined by the measurement of the velocity of sound in the gas. The velocity of sound, v, in gas is given by the expression—

$$v = \sqrt{\frac{P\gamma}{d}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P = pressure of the gas, d = density of the gas, γ = ratio of specific heat at constant pressure to specific heat at constant volume.

The relationship between the velocity of sound and the wavelength of the sound is given by the expression

$$v = n\lambda \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where v = velocity of sound, n = frequency of sound, λ = wavelength of sound.

Thus,
$$n\lambda = \sqrt{\frac{P\gamma}{d}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and therefore,
$$\gamma = \frac{n^2\lambda^2 d}{P} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The measurement of the frequency and wavelength of a note produced in a gas is usually made by a method introduced by Kundt and Warburg. For experimental details of this method reference should be made to a textbook of practical physics.

By the Use of the Periodic Classification. The position of an element in the Periodic Classification as determined by a consideration of its properties and the properties of its compounds often provides convincing evidence that the correct sub-multiple of the molecular weight has been employed. It is of interest to note that this method is entirely independent of Avogadro's Hypothesis, but at the same time it provides one of the strongest pieces of evidence of the validity of that Hypothesis. The Periodic Classification will be discussed in more detail later (*see* p. 38).

Determination of Atomic Weight when the Equivalent Weight is known

Cannizzaro's Method for Elements which Form a Large Number of Gaseous or Readily Volatile Compounds. Cannizzaro stated that the atomic weight of an element was the smallest weight of that element contained in the molecular weight of any of its compounds.

Since the molecular weight, as evaluated from measurements of vapour density, is not exact, the atomic weight calculated from the molecular weight will not be exact. It is, therefore, important to appreciate that the exact atomic weight is the simple multiple of the equivalent weight which most closely approximates to the value of the atomic weight calculated from vapour density measurements. The method of calculation is illustrated by reference to the element carbon as shown opposite.

The equivalent weight of carbon is 3·00, therefore, it is clear that since the smallest weight of carbon found in 1 g molecular weight of any of the compounds quoted in the following table is 12 g, then the exact atomic weight of carbon is 12·00.

Compound of Carbon (either Gaseous or Readily Volatilized)	Vapour Density	Molecular Weight (Vapour Density × 2)	Percentage of Carbon in Compound	Weight of Carbon in 1 g Molecular Weight of the Compound (grammes)
Carbon dioxide . .	22	44	27·3	12
Carbon monoxide .	14	28	42·8	12
Methane . . .	8	16	75·0	12
Ethylene . . .	14	28	86·5	24
Acetylene . . .	13	26	92·3	24
Chloroform . .	60	120	10·04	12
Di-ethyl ether . .	37	74	64·9	48

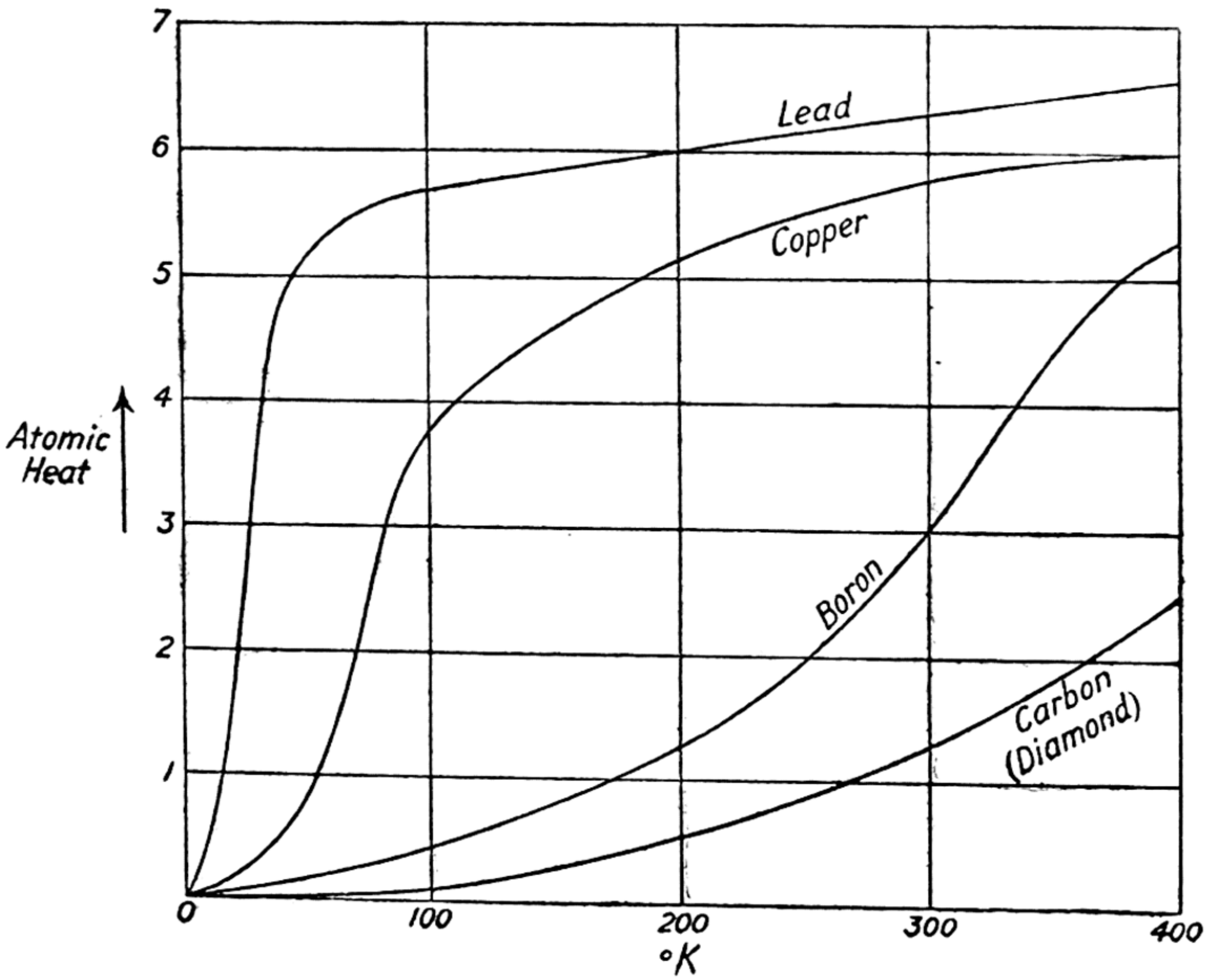

FIG. 9. Variation with Temperature of Atomic Heats for Copper, Lead, Boron and Carbon

Dulong and Petit's Method. Dulong and Petit (1819) found that for most solid elements the *atomic heat* (the product of the specific heat and atomic weight) is of constant value, approximately 6·4. This generalization is the so-called *Law of Dulong and Petit*. The chief exceptions to this rule

are the elements carbon, boron, beryllium and silicon with atomic heats, 1·35, 2·5, 3·5 and 4·7 respectively; these values are determined at 20°C.

The atomic heats of all solid elements approach zero at absolute zero, but at elevated temperatures, which are different for differing elements, the atomic heat increases to a constant value (*see* Fig. 9). Dulong and Petit's method has been utilized for the purpose of fixing atomic weights in a number of doubtful cases. Thus, the equivalent weight of uranium is 39·75, and since a number of its compounds are similar to iron in their chemical reactions it was assumed that its valency was also three, and consequently its atomic weight was calculated to be 119·25. Mendeléeff, however, was unable to find a place in his Periodic Classification for an element with such an atomic weight, and he therefore proposed to adopt double this value, that is 238·5. At a later date the specific heat of uranium was determined to be 0·027, so the action of Mendeléeff in assuming for uranium an atomic weight of approximately 240 was justified. In a similar manner the atomic weight of indium was verified.

In order to determine the approximate atomic weight of an element it is necessary therefore to measure the specific heat of the solid element in the temperature range within which the atomic heat is of constant value and then to divide 6·4 by this figure. In order to calculate the exact atomic weight a determination of the equivalent weight must also be made. The following example will help to make clear the method of calculation.

Numerical Example

It is required to calculate the atomic weight of copper whose specific heat is 0·09232 and equivalent weight is 31·785.

$$\text{By Dulong and Petit's rule} \qquad \frac{6{\cdot}4}{0{\cdot}09232} = \text{approximate atomic weight of copper}$$

$$= 69{\cdot}33$$

$$\text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent weight}} = \frac{69{\cdot}33}{31{\cdot}785}$$

$$= 2{\cdot}181$$

The valency must, however, be a whole number and therefore the valency of copper $= 2$

However, atomic weight $=$ Equivalent weight $\times$ Valency

Therefore, exact atomic weight of copper $= 31{\cdot}785 \times 2$

$$= \underline{\underline{63{\cdot}57}}$$

By the Application of the Law of Isomorphism. This method depends upon the fact that compounds of similar but not identical composition

crystallize in similar forms and that elements of similar chemical characteristics may replace one another in crystalline compounds (*see* p. 128).

Compounds which crystallize in the same form are said to be *isomorphous* and the phenomenon is termed *isomorphism*. For example, rubidium chloride is isomorphous with potassium chloride, so that since the molecular formula of potassium chloride is KCl, then that of rubidium chloride is RbCl and the atomic weight of rubidium can be calculated from the results of the chemical analysis of rubidium chloride.

CHAPTER 3

THE PERIODIC CLASSIFICATION OF THE ELEMENTS AND ATOMIC STRUCTURE

ONE of the most valuable parts of chemical theory is the so-called *Periodic Law*. In its modern form this law states that *the properties of the elements depend upon the structures of their atoms*. This variation occurs in a periodic manner and involves a regular repetition of characteristic

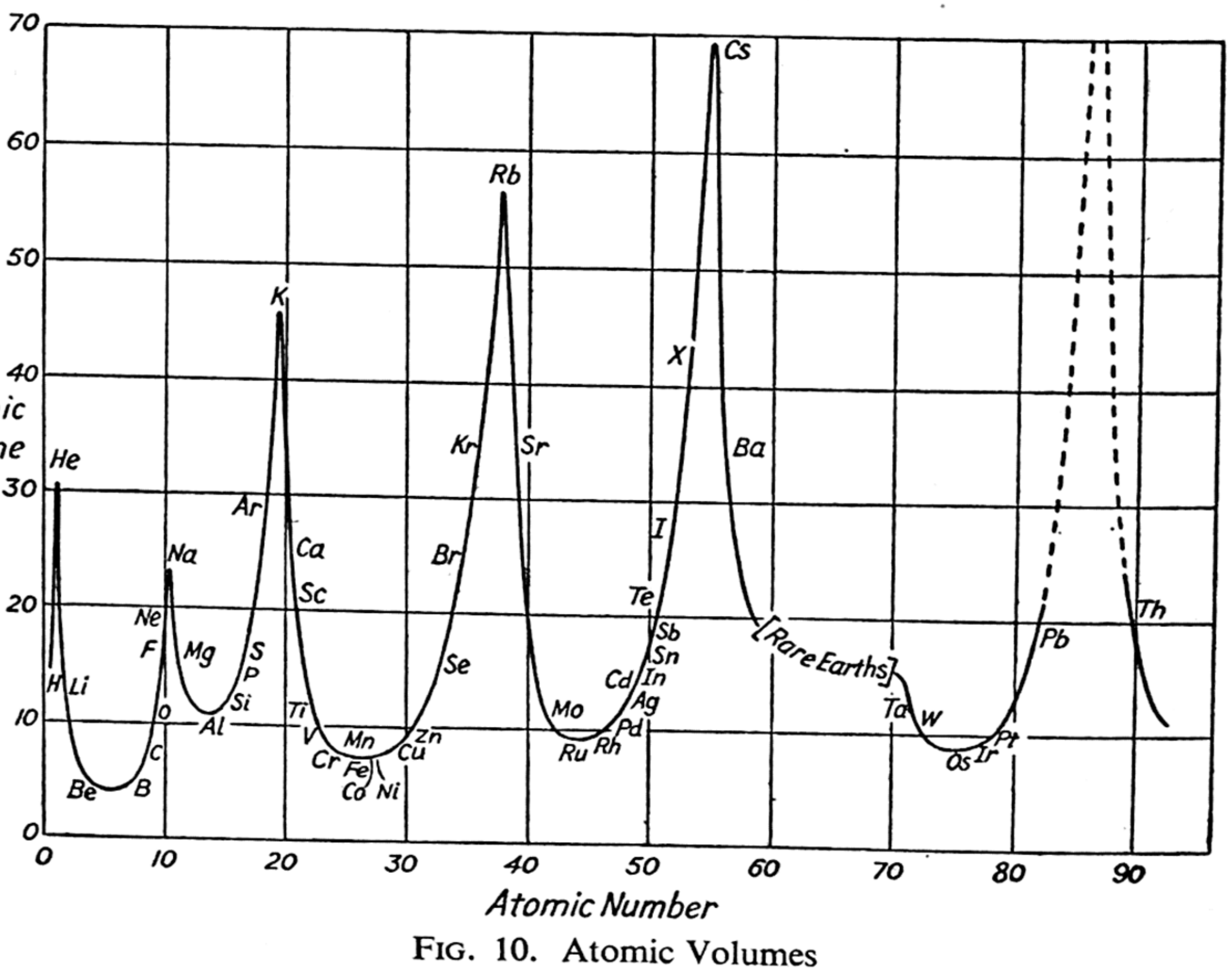

FIG. 10. Atomic Volumes

properties. Thus, for example, if atomic volume in the solid state (i.e. atomic weight/density) is plotted against atomic number as shown in Fig. 10, an unmistakable periodicity is exhibited. This periodicity is again apparent in the occurrence of the group of rare gases having atomic numbers 2, 10, 18, 36, 54 and 86, these gases all being outstanding for their lack of chemical reactivity.

The first systematic classification of the elements was made by

Döbereiner in 1829. He pointed out that many chemically related elements formed well-marked groups of three or *triads*, the middle member of each triad having an atomic weight which was roughly midway between the other two. This is shown below—

Element . . .	Cl	Br	I	Ca	Sr	Ba	S	Se	Te
Atomic weight . .	35·5	80	127	40	87	137	32	79	128
Difference . . .	44·5	47		47	50		47	49	

In addition, Döbereiner pointed out that there were certain groups of three elements with more or less the same atomic weight, for example—

Iron	55·85
Cobalt	58·94
Nickel	58·69

This grouping of elements into trios was known as *Döbereiner's Law of Triads*.

In 1859, Dumas went a step further and arranged certain elements into series (or groups) as shown below. It should be noted that the increments of atomic weight are no longer uniform in the same series, but are often the same for two or more separate series.

	N		P		As		Sb
Atomic weight . . .	14		31		75		120
Difference		17		44		45	

	F		Cl		Br		I
Atomic weight . . .	19		35·5		80		127
Difference		16·5		44·5		47	

	Mg		Ca		Sr		Ba
Atomic weight . . .	24		40		87		137
Difference		16		47		50	

Greater progress than this was hardly to be expected at the time since there was so much uncertainty as to the correct values for the atomic weights of the elements. In 1857 however, Cannizzaro drew the attention of chemists to Avogadro's Hypothesis, proposed in 1811, by the application of which it was possible to fix the atomic weights so that the possibility existed for further progress in the classification of the elements.

TABLE 2

The Periodic Classification of the Elements (after Bohr)

Period	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group O
1				H 1				He 2
2	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	A 18

	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	O
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Cb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92	Np † 93											

* *Rare Earth Metals*

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
58	59	60	61	62	63	64	65	66	67	68	69	70	71

† *Transuranic Elements*

Np	Pu	Am	Cm	Bk	Cf
93	94	95	96	97	98

The first step in this direction was made by Newlands in 1863 when he proposed the *Law of Octaves*. Newlands found that if the elements were arranged in the order of their atomic weights the members of a given family of elements recurred at regular intervals, as in the case of octaves in the musical scale. Thus, the third element resembled the eleventh and nineteenth elements, and so on. Newland's classification proved satisfactory, more or less for the first two *octaves*, but broke down after the twentieth element. Nevertheless, the underlying idea in Newland's classification was a fundamental one.

The next step was taken simultaneously, and independently, in 1871 by Mendeléeff and Lothar Meyer. These two workers proposed a table with eight vertical groupings and a number of horizontal rows or periods.

In the modern version of the Periodic Table as shown opposite, the first period is of very short duration, containing only the two gases hydrogen and helium; this period is followed by two "short periods" each containing eight elements, two "long periods" containing eighteen elements each, then a very long period of thirty-two elements, and finally an incomplete period. It will be noted that this modern version of the Periodic Table contains nine groups, not eight as proposed by Mendeléeff and by Lothar Meyer; this ninth group contains the inert gases and was added subsequent to the discovery of these inert gases in 1894 onwards.

It is to be noted that in the case of three pairs of elements the order of increasing atomic weight has been reversed in drawing up the Periodic Table; these elements are argon and potassium, cobalt and nickel, and tellurium and iodine. This reversal of order is justified since in the naturally occurring specimens of these elements, the atomic weight of the naturally occurring mixture of isotopes is greater for the element of lower atomic weight in each of these pairs of elements than for the element of higher atomic weight.

The position of hydrogen is difficult to fix; it is sometimes placed in Group I, not because it is an alkaline element, but rather that placing it in any other group would be still more inappropriate. In Periods 4, 5, 6 and 7 the groups are divided into two sub-groups, the *a* and *b* Sub-Groups. The elements of Periods 2 and 3 usually resemble the elements of the same group in *either* Sub-group *a or* Sub-group *b*, *but not both sub-groups*. Thus, the alkali metals lithium and sodium strongly resemble the metals potassium, rubidium and caesium (three metals in the I*a* Sub-group), but do not very much resemble the three metals, copper, silver and gold (three metals in the I*b* Sub-group). The elements found in Periods 2 and 3 are often referred to as "typical elements," or elements in the "main group."

In a similar manner the two typical elements fluorine and chlorine in the main group more closely resemble the two elements bromine and iodine which occur in the VII*b* Sub-group, rather than the metallic elements manganese, technitium and rhenium found in the VII*a* Sub-group.

Elements at the left-hand side and in the centre of the Periodic Table are metals, whilst those found on the right-hand side of the table are non-metals. Certain elements (e.g. boron, silicon, germanium, arsenic, antimony, tellurium and polonium) exhibit intermediate properties and constitute an intermediate zone; these elements are termed *metalloids*.

Each of the long periods of the Periodic Table (Table 2) contains a group of ten elements which is often referred to as a "transitional series." In such series there is a gradual change in properties from one element to the next, although such differences are less marked than those between successive typical elements in Periods 2 and 3. In general, the members of any one transitional series are characterized by a general similarity.

Certain pairs of elements found in different groups of the Periodic Table are characterized by a general similarity in properties; thus, lithium resembles calcium, beryllium resembles aluminium, and boron resembles silicon. In each of these cases the second member of each pair possesses an extra electron in the outermost shell with a corresponding greater positive charge on the nucleus, so that it is less electropositive than the first member of the pair. On the other hand, the second member of each pair has the greater atomic volume and this renders the element more electropositive. It thus follows that these two factors more or less offset one another with the result that although the valencies of the members of each pair are different, their general characteristics and those of their compounds are similar.

CATHODE RAYS AND POSITIVE RAYS

Although, under normal conditions, air and other gases are regarded as poor conductors of electricity, at reduced pressures electrical conduction occurs more readily and is associated with a number of visible effects.

If a high tension discharge is passed through a discharge tube undergoing evacuation it is found that as the pressure is progressively reduced inside the tube, the glow, which at first surrounds the cathode, gradually detaches itself from this electrode, the space between the cathode and the glow being known as the "Crookes dark space." As the pressure is further reduced the size of the Crookes dark space increases until, at a sufficiently low pressure (i.e. 0·01—0·001 mm of mercury), it occupies the whole of the tube. At this stage the glass wall of the discharge tube opposite to the cathode is found to fluoresce. This phenomenon of fluorescence is produced by the *cathode rays* travelling in straight lines normal to the surface of the cathode (*see* Fig. 11), as may be demonstrated by the production of a shadow caused by interposing an opaque object between the cathode and the end of the discharge tube. These cathode rays also possess sufficient momentum to cause the rotation of a small paddle wheel placed inside the evacuated discharge tube.

Sir J. J. Thomson showed that these cathode rays were electrically

charged since they were capable of being deflected by electrostatic or magnetic fields. As the cathode rays are projected from the cathode they must be negative in sign and this can be proved by allowing them to fall upon an insulated metal plate which then acquires a negative charge.

It has been shown that cathode rays consist of extremely small, negatively charged particles expelled with a high velocity from the cathode. To these particles the name of *electrons* has been given.

Using a deflection method Sir J. J. Thomson caused a stream of cathode rays to traverse a crossed electric and magnetic field and, by measuring the deflections produced, calculated the ratio of the charge of the electron, e, to the mass of the electron, m, as follows. If magnetic field of strength H is applied at right angles to the direction of the electron stream, then the magnetic force exerted on each electron is Hev if the charge on the electron

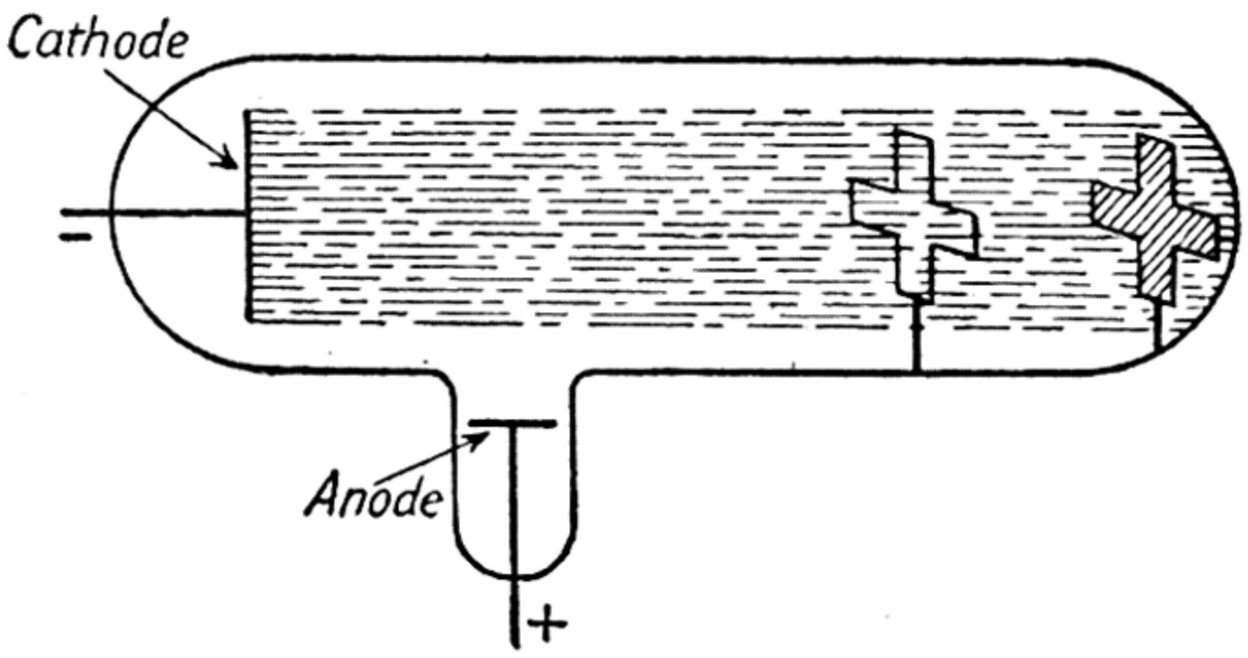

FIG. 11. Cathode Rays

is e, the mass of the electron m and the linear velocity of the electron v. Under the influence of this magnetic force the electrons will describe a circular path of radius, r, in which the centrifugal force just balances the magnetic force, thus—

$$Hev = mv^2/r \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Therefore,

$$e/m = v/Hr \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

The radius of curvature r of the cathode ray stream when deflected by the magnetic field of strength H is capable of measurement, but before the ratio e/m may be evaluated it is necessary to know the velocity of the electron stream, v. This may be calculated as follows.

An electric field of strength X acts upon an electron with a force Xe. If both magnetic and electric fields are applied simultaneously, but in opposition, the electron stream will not suffer deflection provided that the magnetic and electric forces are equal. When this obtains,

$$Hev = Xe \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Therefore

$$v = X/H \quad . \quad . \quad . \quad . \quad (2a)$$

It is thus possible to determine the velocity of the electrons from the ratio of the strengths of the two fields, if expressed in suitable units.

It was found that the ratio, e/m, for the electron was the same no matter of what material the cathode was made, and no matter what the nature of the residual gas in the discharge tube. According to recent determinations the ratio of charge to mass of the electron is $1{\cdot}758 \times 10^7$ e.m. units per g (i.e. $1{\cdot}758 \times 10^8$ coulombs per g), provided that the electron velocity is not too high. Assuming that the electron and the hydrogen ion have the same charge, then the mass of the electron is 1/1836 part of the mass of a hydrogen atom. It follows, therefore, that the electron is a common constituent of all matter, and always possesses the same properties.

Just as cathode rays are emitted from the cathode surface under the influence of an electrical potential, so rays are also given off by the anode provided that the pressure inside the discharge tube is not too low. These

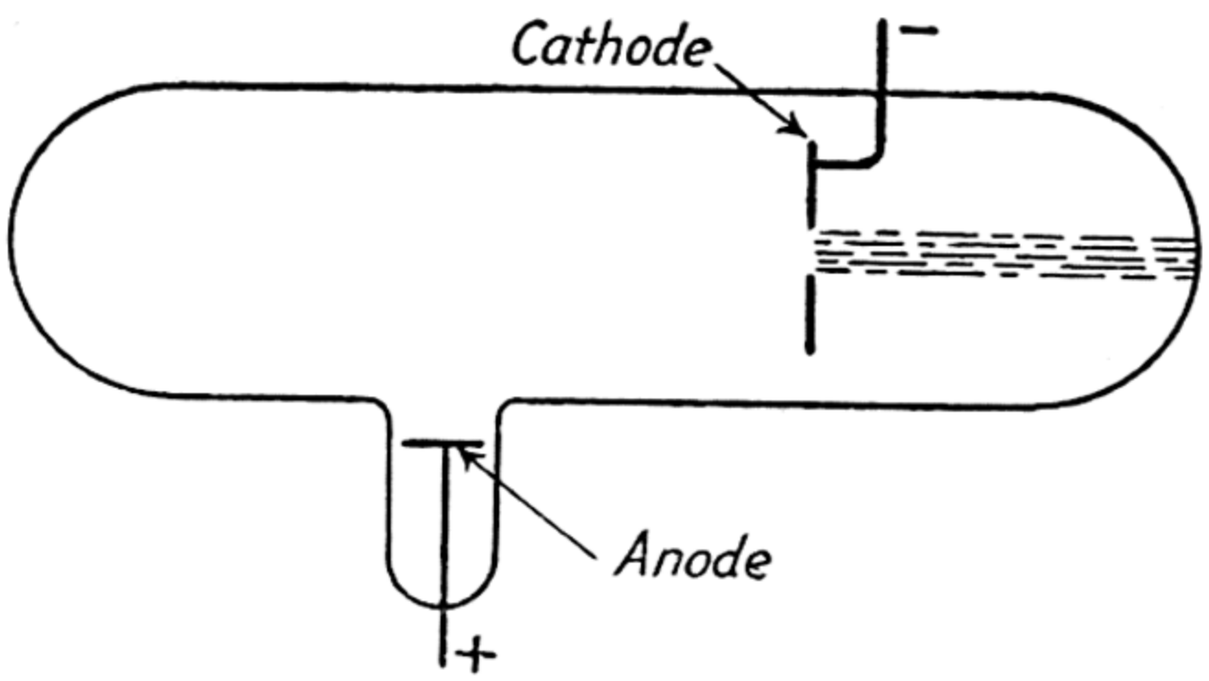

FIG. 12. Anode Rays

rays originally were known as *canal rays*, but now are invariably termed *positive rays* since they are positively charged and suffer deflection in the opposite direction to that expected for cathode rays. Positive rays may be detected by using a perforated disc as cathode when the positive rays will be observed as a narrow beam emerging from the side of the cathode opposite to the anode (*see* Fig. 12). Positive rays differ from cathode rays in that they are always associated with material particles, and also that whereas anode rays appear to originate in the glow surrounding the Crookes dark space, cathode rays actually start from the cathode. Sir J. J. Thomson determined the ratio e/m for positive rays by the same method as that employed for cathode rays but found that this ratio was not constant, as was the case for cathode rays, but was dependent upon the nature of the residual gas in the discharge tube.

The Inter-relationship of Mass, Velocity and Energy. In quoting above the numerical value of the ratio e/m for an electron as $1{\cdot}758 \times 10^7$ e.m. units per gramme, the proviso was made that the velocity of the electron stream should not be too high. In Sir J. J. Thomson's classic experiments the velocity of the electron stream was approximately 3×10^9 cm/sec, that is about one-tenth the velocity of light. But the velocity of the electron

stream varies with variation of the applied potential, being proportional to the square root of the potential gradient.

Thus, as the velocity of the electron stream increases, the numerical value of the ratio e/m decreases, due, not to a decrease in the value of the charge, but to an increase in the value of the mass in accordance with relativity theory. In accordance with the theory of relativity the actual mass of a particle, m, moving with a velocity, v, is given by the expression—

$$m = m_0 / \sqrt{1 - (v/c)^2} \quad . \quad . \quad . \quad (3)$$

where m_0 = the mass of the particle at rest, that is, the so-called "rest mass," c = the velocity of light.

From (3) it follows that the actual mass of a particle (in this case an electron) increases as its velocity increases. For velocities lower than 10^9 cm/sec the numerical value of the actual mass differs from the rest mass by not more than 1 per cent so that at relatively low velocities the mass of an electron may be regarded as more or less constant and it is this value which is 1/1836 of the mass of a hydrogen atom. Thus, since the mass of a moving body increases as its velocity increases, there is an equivalence between increase in kinetic energy (i.e. the increase in the energy of motion of the body) and the increase in mass. In other words, energy and mass are interconvertible. Einstein concluded that the amount of energy, E, equivalent to mass, m, is given by the equation—

$$E = mc^2 \quad . \quad . \quad . \quad . \quad (4)$$

where c = the velocity of light (i.e. $2{\cdot}9977 \times 10^{10}$ cm/sec).

From (4) it will be observed that any change of energy, E, is associated with a change of mass equal to E/c^2 so that the Law of Conservation of Mass is therefore only strictly valid provided that there is no energy change involved in the process under consideration. Since in chemical reactions the change in mass (equivalent to the heat change involved) is so extremely small as to be incapable of determination by the ordinary processes of manipulation the apparent verification of the Law of Conservation of Mass has been accepted. This is emphasized by the fact that 1000 calories (i.e. $4{\cdot}18 \times 10^{10}$ ergs) are equivalent to only $4{\cdot}6 \times 10^{-7}$ g, which is obviously so small as to be incapable of experimental determination.

The Charge, Mass and Size of the Electron. The magnitude of the electronic charge may be evaluated from the expression—

$$e = \frac{F}{N} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where F = the Faraday (96 500 coulombs), N = the Avogadro number ($6{\cdot}025 \times 10^{23}$).

Thus, since 96 500 coulombs = 9650 e.m. units, then—

$$e = \frac{9650 \times 2{\cdot}9977 \times 10^{10}}{6{\cdot}025 \times 10^{23}}$$
$$= 4{\cdot}800 \times 10^{-10} \text{ e.s. units}$$

The numerical value of the ratio e/m has been quoted above as

$$e/m = 1{\cdot}758 \times 10^{7} \text{ e.m. units}$$
$$= 1{\cdot}758 \times 10^{7} \times 2{\cdot}9977 \times 10^{10} \text{ e.s. units}$$
$$= 5{\cdot}270 \times 10^{17} \text{ e.s. units}$$

Since, as also shown above, the electronic charge is

$$e = 4{\cdot}800 \times 10^{-10} \text{ e.s. units}$$

then, $$m = 4{\cdot}800 \times 10^{-10}/5{\cdot}270 \times 10^{17} \text{ e.s. units}$$
$$= 9{\cdot}11 \times 10^{-28} \text{ g}$$

An approximate value of the radius of an electron is given by the expression

$$r = e^2/mc^2 \quad . \quad . \quad . \quad . \quad (6)$$

where e = the electronic charge, m = the mass of the electron, c = the velocity of light.

Substituting the values quoted above

$$r = 2{\cdot}8 \times 10^{-13} \text{ cm (approximately)}$$

The Proton. As stated above the numerical value of the ratio e/m for positive rays is not constant but varies with the nature of the residual gas remaining in the discharge tube. As a result of a detailed study of positive rays it has been established that the lightest positively charged particle has a mass almost equal to that of a hydrogen atom, that is, a mass about 1835 times as great as that of the electron. This particle, to which the name *proton* has been given, is a positive hydrogen ion, that is a hydrogen atom which has lost an electron.*

THE NUCLEAR THEORY OF THE ATOM

It was found that if that part of the wall of a discharge tube opposite to the cathode be made from thin metal foil instead of glass the cathode rays will pass through the foil, without the latter suffering perforation, and out into the atmosphere beyond. This could only happen if the size of the electron is very much smaller than that of the atom as a whole and if the greater part of the atom is more or less "transparent" to electrons.

* The proton, that is, the *gaseous* hydrogen ion should not be confused with the hydrogen ion in solution which is a combination of a proton and a molecule of the solvent (e.g. H_3O^+ in aqueous solution).

Emphasis is given to this view by the fact that knowing the diameters of gaseous molecules, and by application of the kinetic theory, it is possible to calculate the probable number of encounters with molecules an electron might have during the period of its passage through the gas; the results show that the greater portion of an atom must be "transparent" to electrons.

Arising from these and similar related phenomena, the modern theory of atomic structure, based on the nuclear theory, was proposed by Lord Rutherford who suggested that the positive charge of an atom is concentrated at a central point which is surrounded by negative particles. The behaviour of radioactive substances has been of very considerable assistance in elucidating the structure of the atom, and in this connexion the so-called "alpha-particle," emitted by radioactive substances, has been of especial value.

The first reported observation of radioactivity was by Becquerel in 1895, who noted the fogging effect of uranium minerals on photographic plates—even when the latter were carefully wrapped in black paper—and their power of ionizing the air so that an electric charge on an electroscope will leak rapidly away through the air if a radioactive substance is placed near it. It is to the spontaneous emission of radiation of this type that the name "radioactivity" is given.

Radioactive substances emit radiations of three types known respectively as *alpha-particles*, *beta-rays* and *gamma-rays* (α-particles, β-rays and γ-rays). These three kinds of radiation differ amongst themselves in regard to penetrating power, influence of magnetic field, and ability to ionize air. The penetrating power of α-particles is about 1/100 that of γ-rays, whilst that of β-rays varies from 1/10 upwards that of γ-rays. Under the influence of a magnetic field α-particles are deflected slightly in such a direction as to indicate that they are positively charged. Under the influence of the same magnetic field β-rays undergo considerable deflection in the opposite direction showing that they are negatively charged, whilst γ-rays are undeflected.

In regard to ionizing power, α-particles are most effective, being approximately one hundred times as powerful as β-rays, and the latter approximately one hundred times as powerful as γ-rays.

Alpha-particles

As stated above it has been shown that under the influence of a magnetic field α-particles are deflected slightly in such a direction as to indicate that they are positively charged. By superimposing magnetic and electric fields, the deviation of the path of an α-particle may be observed and the value of e/m evaluated. The numerical value of this ratio for α-particles is $4{\cdot}813 \times 10^3$ e.m. units/g. The charge carried by an α-particle is approximately $9{\cdot}3 \times 10^{-10}$ e.s. units, which is roughly twice that of an electron. The α-particles must, therefore, each carry two unit charges. Since 1 g-ion

of hydrogen carries $9{\cdot}650 \times 10^3$ e.m. units, and the α-particle carries two charges, it follows that the mass of the α-particle must be approximately four times that of the hydrogen atom. In fact, it is now known that α-particles are helium atoms each carrying two positive charges.

Like cathode rays, α-particles are capable of penetrating thin sheets of metal foil and in doing so most of the α-particles do not suffer any appreciable deflection, but a small proportion are scattered through large angles (i.e. more than 90°). Lord Rutherford suggested that this scattering must be due to the encounter of α-particles and the atoms of the metal making up the foil, and in particular, the large-angle scattering must result from a *single* encounter of an α-particle and a metal atom (*see* Fig. 13). Thus Lord Rutherford argued that these observations could be explained by assuming that the whole of the positive charge associated with an atom is concentrated at a very small, central nucleus which is surrounded at a relatively large distance by electrons, often termed "extra-nuclear electrons" in this connexion, which, being negatively charged, provide electrical neutrality to the atom as a whole.

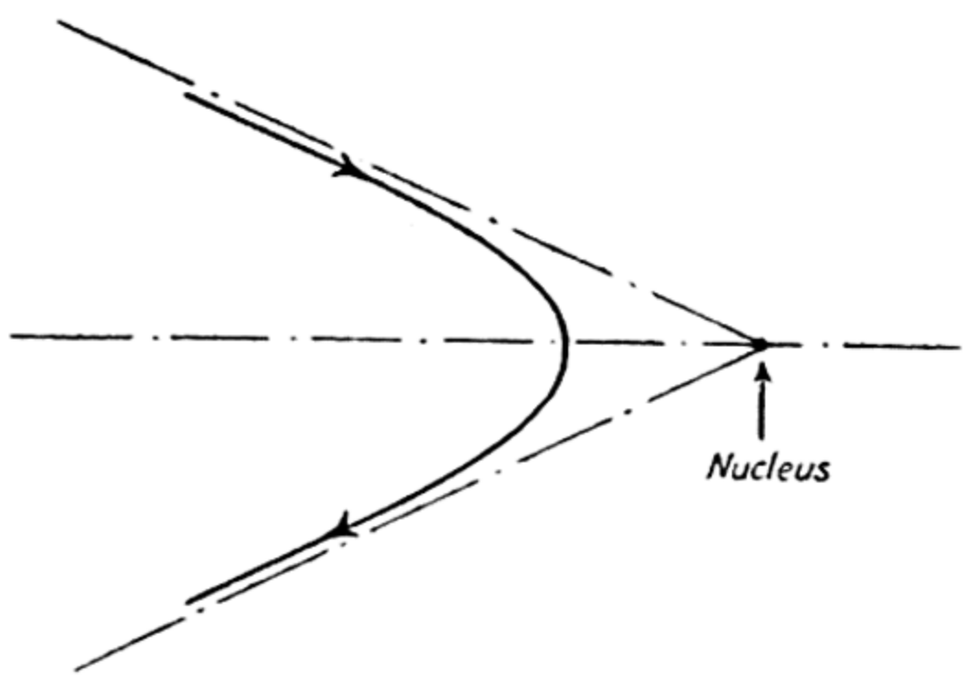

FIG. 13. Scattering of α-particle by an Atomic Nucleus

With this picture in mind it becomes clear why a swiftly moving α-particle will not be deflected to any appreciable extent by an electron since the latter has a very much smaller mass, so that the majority of α-particles may pass through an atom without suffering any appreciable scattering. On the other hand, should an α-particle enter the strong electric field in the immediate vicinity of the nucleus it will obviously suffer violent deflection. It is important to appreciate that the ability of positively charged nuclei to repel other positively charged nuclei is a fundamental property. In a similar manner, electrons, being negatively charged, will repel other electrons.

The picture which has been built up is that every atom consists of a small, heavy nucleus of the order of 1×10^{-5} to 1×10^{-4}Å* in diameter (i.e. 1×10^{-13} to 1×10^{-12} cm). The nucleus is surrounded largely by an "empty" region of the order of 1 Å diameter in which the electrons circulate around the nucleus in a manner similar to that in which the planets circulate around the sun. This is the so-called *nuclear theory of the atom.*

The "transparent" nature of the atom is made more obvious when it is noted that if nuclei could be packed together side by side, a form of matter would be produced having the phenomenal density of approximately

* The Ångström unit is a unit of length employed in the measurement of very small lengths. 1 Å $= 1 \times 10^{-8}$ cm.

1×10^{12} g/cm^3. The tendency for such packing would appear to occur at the extremely high temperatures and pressures that obtain in the centres of stars, and it has been calculated that the density of one star is of the order of $6{\cdot}1 \times 10^4$ g/cm^3 (i.e. approximately 1 ton/in.^{3}).

X-rays

In 1895 Röntgen discovered that when cathode rays produced in a highly evacuated discharge tube were allowed to fall upon matter, new radiations were produced. These radiations he called *X-rays*. In order that the X-rays may readily be deflected out of the discharge tube it is usually more convenient if the cathode rays are allowed to impinge upon a metal target known as the *anti-cathode* (*see* Fig. 14).

X-rays have been found to exhibit much greater penetrating power than cathode rays. They are also, like α-particles, capable of ionizing air and

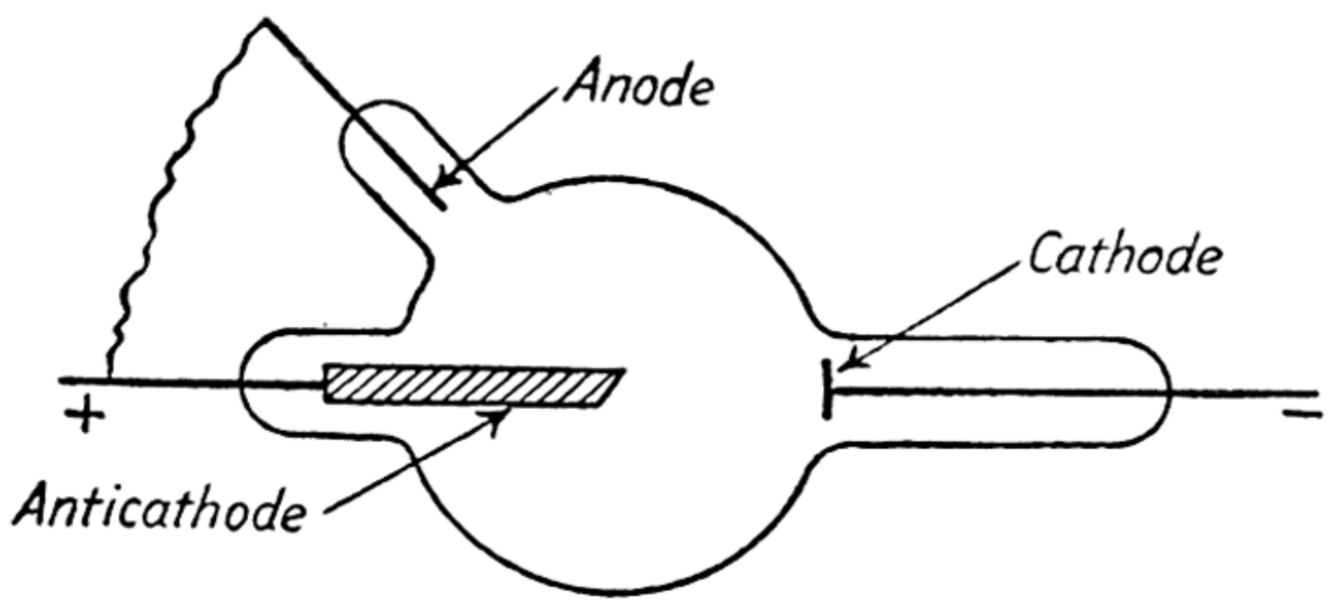

FIG. 14. X-ray Tube

other gases, but differ from α-particles in that they are not influenced by magnetic and electric fields. They are in this respect therefore similar to the γ-rays emitted by radioactive substances in that both X-rays and γ-rays are not corpuscular, but consist of electromagnetic radiations, the wave-length of γ-rays being the shorter of the two.

In general, the X-rays as radiated from the anti-cathode of a discharge tube are heterogeneous, that is the X-ray spectrum is not continuous but consists of a number of characteristic lines or series (or groups) of lines. Two series known respectively as the K- and L-series are of particular importance, the K-series being much harder than the L-series (i.e. of much greater penetrating power). With the object of making a comparison of the X-ray spectra of different elements it is usual to compare measurements made on a specific line in the different spectra; from the position of the line of the spectrum these measurements permit of the calculation of the frequency of this particular radiation.

In 1913, H. G. J. Moseley found that with variation of the material used for the anti-cathode, so that elements of decreasing atomic weight are employed, the wave-length of the X-rays produced undergoes a corresponding decrease, and simultaneously the K-series becomes more difficult

TABLE 3

International Atomic Weights, 1947

	Symbol	*Atomic No.*	*Atomic Weight*		*Symbol*	*Atomic No.*	*Atomic Weight*
Aluminium	Al	13	26·97	Neon	Ne	10	20·183
Antimony	Sb	51	121·76	Nickel	Ni	28	58·69
Argon	A	18	39·944	Niobium (Columbium)	Nb	41	92·91
Arsenic	As	33	74·91				
Barium	Ba	56	137·36	Nitrogen	N	7	14·008
Beryllium	Be	4	9·02	Osmium	Os	76	190·2
Bismuth	Bi	83	209·00	Oxygen	O	8	16·0
Boron	B	5	10·82	Palladium	Pd	46	106·7
Bromine	Br	35	79·916	Phosphorus	P	15	30·98
Cadmium	Cd	48	112·41	Platinum	Pt	78	195·23
Caesium	Cs	55	132·91	Potassium	K	19	39·096
Calcium	Ca	20	40·08	Praseodymium	Pr	59	140·92
Carbon	C	6	12·01	Protoactinium	Pa	91	231·0
Cerium	Ce	58	140·13	Radium	Ra	88	226·05
Chlorine	Cl	17	35·457	Radon	Rn	86	222·0
Chromium	Cr	24	52·01	Rhenium	Re	75	186·31
Cobalt	Co	27	58·94	Rhodium	Rh	45	102·91
Copper	Cu	29	63·54	Rubidium	Rb	37	85·48
Dysprosium	Dy	66	162·46	Ruthenium	Ru	44	101·7
Erbium	Er	68	167·2	Samarium	Sm	62	150·43
Europium	Eu	63	152·0	Scandium	Sc	21	45·10
Fluorine	F	9	19·00	Selenium	Se	34	78·96
Gadolinium	Gd	64	156·9	Silicon	Si	14	28·06
Gallium	Ga	31	69·72	Silver	Ag	47	107·88
Germanium	Ge	32	72·60	Sodium	Na	11	22·997
Gold	Au	79	197·2	Strontium	Sr	38	87·63
Hafnium	Hf	72	178·6	Sulphur	S	16	32·066
Helium	He	2	4·003	Tantalum	Ta	73	180·88
Holmium	Ho	67	164·94	Tellurium	Te	52	127·61
Hydrogen	H	1	1·008	Terbium	Tb	65	159·2
Indium	In	49	114·76	Thallium	Tl	81	204·39
Iodine	I	53	126·92	Thorium	Th	90	232·12
Iridium	Ir	77	193·1	Thulium	Tm	69	169·4
Iron	Fe	26	55·85	Tin	Sn	50	118·7
Krypton	Kr	36	83·7	Titanium	Ti	22	47·9
Lanthanum	La	57	138·92	Tungsten	W	74	183·92
Lead	Pb	82	207·21	Uranium	U	92	238·07
Lithium	Li	3	6·94	Vanadium	V	23	50·95
Lutecium	Lu	71	174·99	Xenon	Xe	54	131·3
Magnesium	Mg	12	24·32	Ytterbium	Yb	70	173·04
Manganese	Mn	25	54·93	Yttrium	Y	39	88·92
Mercury	Hg	80	200·61	Zinc	Zn	30	65·38
Molybdenum	Mo	42	95·95	Zirconium	Zr	40	91·22
Neodymium	Nd	60	144·27				

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to excite. From his measurements, Moseley was able to demonstrate the existence of a quantitative relationship between the frequency ν of a specific line in the given series in the X-ray spectrum and the so-called *atomic number Z* of the element in question.

The Atomic Number

The atomic number is, with certain few exceptions, the number which may be apportioned to an element if all the elements are arranged in order of increasing atomic weight, starting with hydrogen equal to unity. Thus Table 3 opposite gives the atomic weights and the corresponding atomic

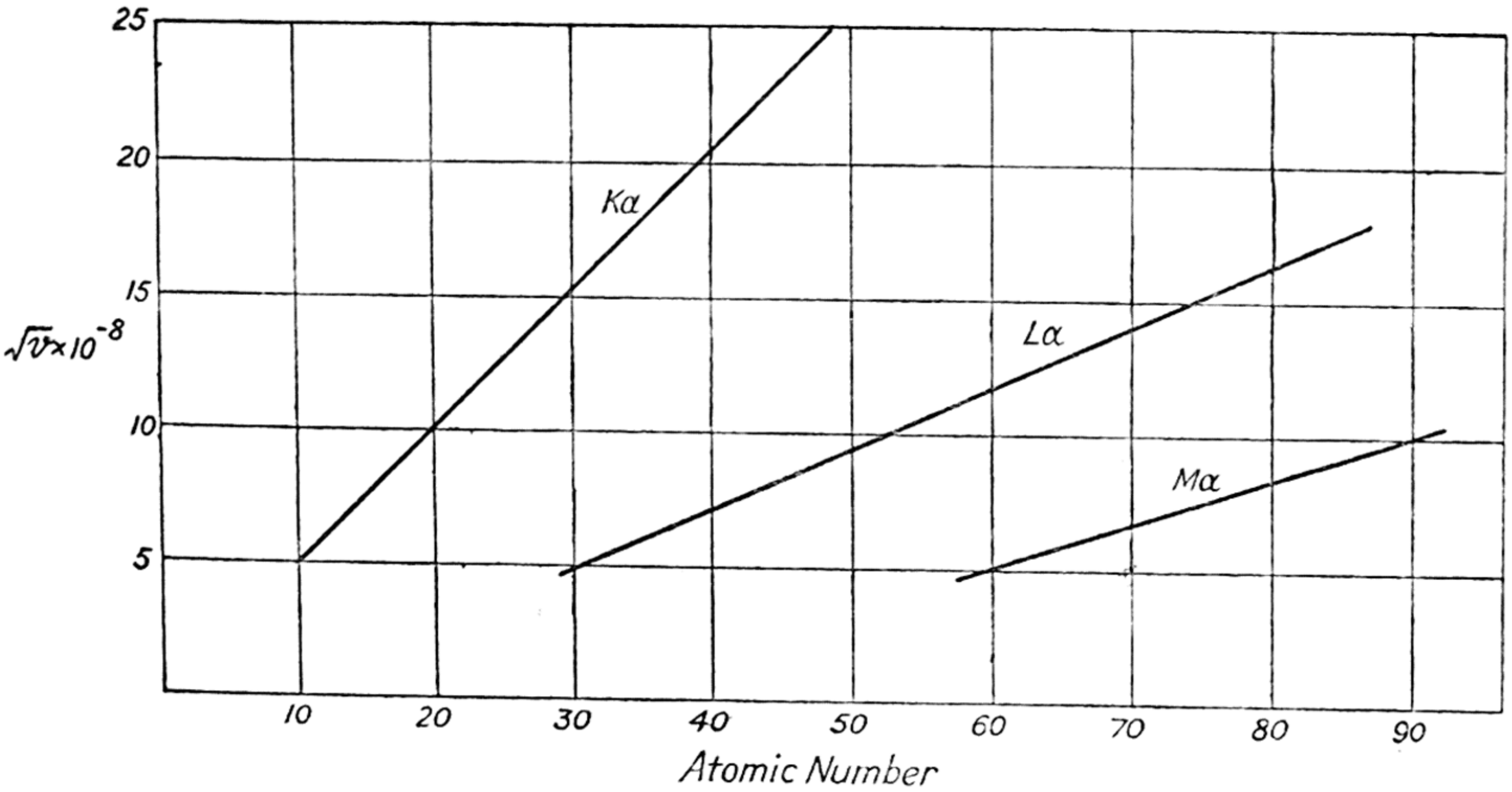


FIG. 15. Relationship of Frequency of Characteristic X-rays and Atomic Numbers

numbers of the elements. The mathematical expression of the relationship between the frequency, ν, and the atomic number, Z, is as follows—

$$\sqrt{\nu} = a(Z - \sigma) \quad . \quad . \quad . \quad . \quad (7)$$

where ν = frequency of specific line within any particular X-ray spectrum, Z = atomic number of the element in question, a = proportionality constant, σ = constant which is the same for all the lines in a given series. Thus for the K_α-line (the strongest line in the K-series) $\sigma = 1{\cdot}0$; whilst for the L_α-line (the strongest line in the L-series) $\sigma = 7{\cdot}4$.

If the square root of the frequency of the characteristic line in a given series is plotted against the atomic numbers of the elements giving rise to the X-rays, a straight line plot is obtained; this is shown in Fig. 15.

When the square root of the frequency is plotted against the atomic *weights* of the elements concerned, no such regularity is apparent. Moseley

therefore deduced that there is some property of the atom—either the atomic number or some quantitative property very closely related to it—which is a fundamental characteristic for each atom, and which increases in a regular manner from one element to the next heavier element. Moseley submitted that this fundamental quantity must represent the magnitude of the charge on the central, positively charged nucleus of the atom.

It is important at this point to emphasize that all nuclei possess positive charges which are equal to, or are simple multiples of, the negative charge possessed by the electron. Thus, the electrical charge of a nucleus of an element with atomic number Z is Ze, since the charge on the electron is $-e$. In other words, the number of positive charges on the atomic nucleus determines the number of electrons in the extranuclear structure, which in

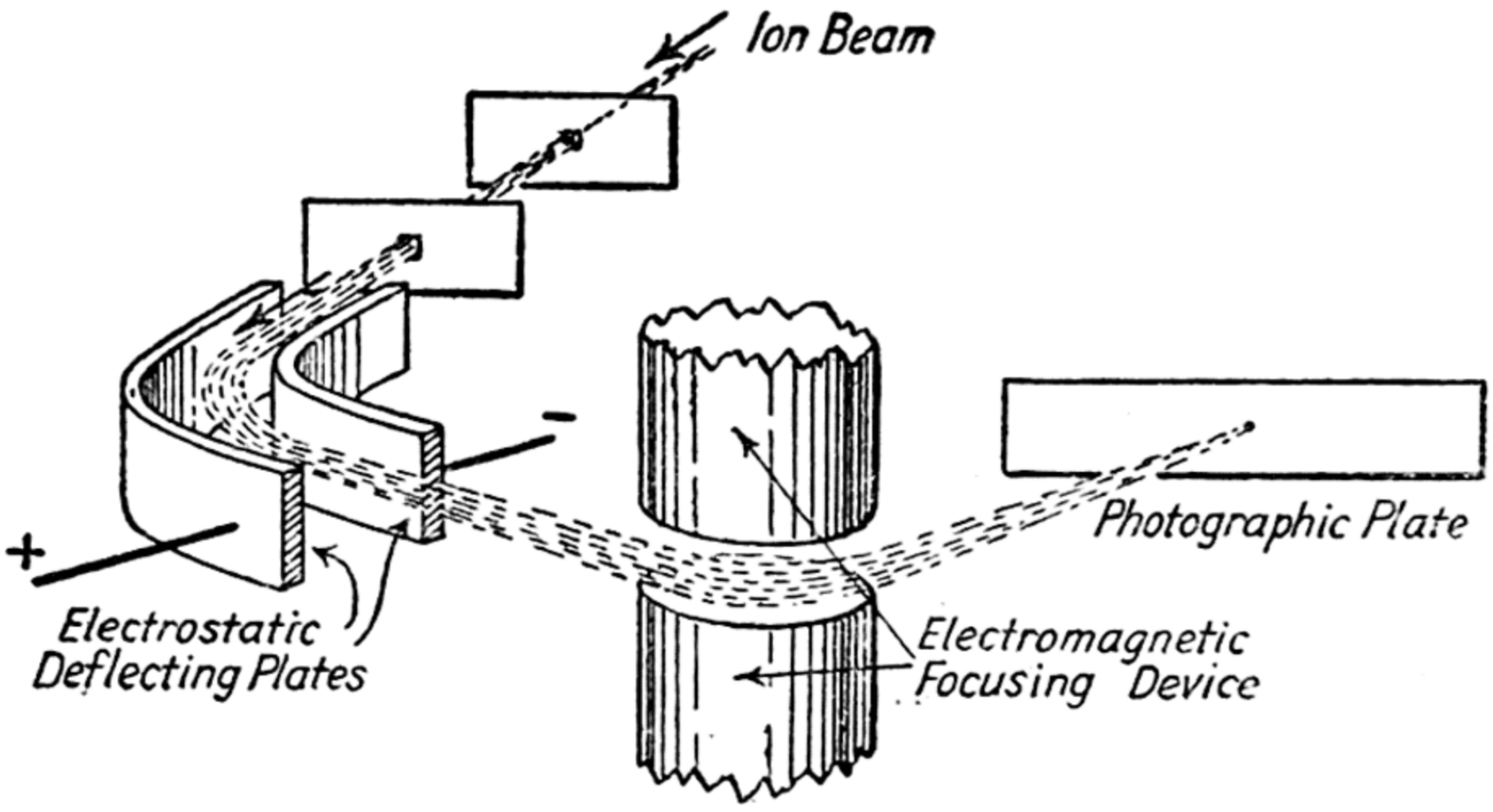


FIG. 16. Focusing Mass Spectrograph

turn determines the chemical properties of the atom in question. *Atomic nuclei are unaffected by chemical processes.* It follows therefore that matter composed of atoms with the same atomic number is composed of a single element regardless of the possible differences in their nuclear structure.

The Constitution of the Atomic Nucleus

The nuclear charge is equal to the atomic number, and also equal to the number of extranuclear electrons necessary for the existence of an electrically neutral atom. Since the electron has only a very small individual mass, the extranuclear electrons only contribute a very small fraction to the mass of the atom as a whole, and therefore, the mass of an atom may be assumed to be concentrated in the nucleus.

The simplest, lightest and smallest nucleus is the proton. This particular nucleus carries unit positive charge and when associated with a single extranuclear electron (carrying unit negative charge) the electrically neutral structure produced constitutes a single hydrogen atom. Thus, since the proton is 1836 times as heavy as the electron, only 1/1836 of the

mass of a hydrogen atom is due to the single planetary electron, the very large, fractional remainder being due to the proton.

By means of recent precision measurements using the focusing mass spectrograph (*see* Fig. 16), a modern form of Sir J. J. Thomson's original apparatus, it has been possible to determine the relative masses of atoms with an accuracy very much greater than that attainable when employing the ordinary chemical methods of atomic weight determination. For example, some of the results obtained by the use of this technique are probably correct to within one part in 10 000. Using this modern form of mass spectrograph, F. W. Aston, A. J. Dempster, and others have determined the *mass number* of the atoms of the elements. The mass number, A, is the number of times the atom in question is greater than the atomic mass unit, a very small unit of mass, $1{\cdot}6603 \times 10^{-24}$ g. In terms of this unit the mass of a proton is 1·00758 mass units.

In atoms heavier than hydrogen the nucleus has a total positive charge greater than unity and is surrounded by a number of electrons circulating in orbits around the nucleus in a planetary manner. If the nuclei of atoms heavier than hydrogen consist only of groups of protons then, neglecting the mass of the extranuclear electrons on account of their small value, the mass number of an atom would be the same as its atomic number. Except in the case of hydrogen this is not so as is demonstrated by Table 4.

TABLE 4

Mass Numbers and Atomic Numbers of Hydrogen, Helium, Lithium, Sodium and Potassium

Element	Mass Number*	Atomic Number
Hydrogen . . .	1	1
Helium . . .	4	2
Lithium . . .	7	3
Sodium . . .	23	11
Potassium . . .	39	19

* Mass numbers are quoted to the nearest whole number.

The difference between the mass number and the atomic number is due to the presence, within the nucleus, of one or more *neutrons*.

The chief characteristic of the neutron which differentiates it from other sub-atomic particles is that it is uncharged (i.e. electrically neutral). The mass of the neutron is 1·00893 mass units. Thus, according to modern views, the nuclei of all atomic species are built up of protons and neutrons, and there are three fundamental sub-atomic particles, protons, neutrons,

and electrons. The number of neutrons, N, in the nucleus of an atom may be found by subtracting the atomic number, Z, from the mass number, A. Thus, since the number of protons is equal to the atomic number, then

$$N = A - Z \quad . \quad . \quad . \quad . \quad (8)$$

In nuclei the combined effect of electric coulomb forces of repulsion between positive charges, and the very short-range forces of attraction between all particles are such that stability can only be obtained when certain combinations of protons and neutrons exist. When the numbers of protons and neutrons are few, as is the case in small nuclei, stability only occurs when these two types of sub-atomic particles exist in roughly equal numbers. On the other hand, in the case of larger nuclei, if stability is to obtain a higher proportion of neutrons appears to be necessary. Identification has been made of about 250 different stable nuclei having mass numbers varying from 1 to 244 and atomic numbers from 1 to 98.

In addition to the proton, electron and neutron other fundamental sub-atomic particles have also been identified. The relationship of these to the three first named will be clear from the following table.

TABLE 5

Fundamental Sub-atomic Particles

Electric Charge on Particle		
Positive	Zero (Neutral)	Negative
Proton (Mass = 1·00758)	Neutron (Mass = 1·00897)	Negative proton (Not known at present)
Positive meson* (Mass = approximately 0·1)	Neutral meson* (Not known at present)	Negative meson* (Mass = approximately 0·1)
Position† (Mass = 0·000548)	Neutrino (A mass of 0·0005 has been proposed. The existence of this particle has, however, not been proved)	Electron (Mass = 0·00548)

* It is possible that mesons provide the fundamental binding forces holding together the protons and neutrons in nuclei.

† The positron is produced by interaction of cosmic rays with matter. Positrons have a very short life as free particles (e.g. 1×10^{-6} sec).

Isotopes. It will be clear that it is possible to alter the mass number of an atom without altering the arrangement of the extranuclear electrons, by adding to the nucleus one or more neutrons, and atoms which vary in this respect will have the same chemical properties since the extranuclear electrons are not involved. Atoms which thus vary with regard to mass number but not in respect of electronic arrangement are termed *isotopes*.

If a sample of an element obtained by chemical means consists of a mixture of its isotopes, the apparent atomic weight as determined by chemical methods is the statistical mean value dependent upon the relative proportions of the isotopes existing in the sample of the element under examination. Thus, for example oxygen, as prepared by the usual chemical methods or as found in nature, contains isotopes of masses 17 and 18 to the extent of 0·04 per cent and 0·20 per cent respectively, the remainder consisting of the isotope of mass 16. The complete definition of the mass unit is $\frac{1}{16}$ of the mass of the predominant isotope of oxygen and its numerical value is $1{\cdot}6603 \times 10^{-24}$ g. In order to distinguish between isotopes it is usual to write the atomic number as a subscript and the mass number as a superscript respectively before the chemical symbol of the element concerned, thus ${}^{16}_{8}\mathrm{O}$. Some typical values of the mass numbers of isotopes are given in Table 6.

TABLE 6

Mass Numbers of Isotopes

Element	Masses of Isotopes
H	1a, 2b
Li	6b, 7a
B	10b, 11a
C	12a, 13b
N	14a, 15b
O	16a, 17c, 18b
Ne	20a, 21c, 22b
Mg	24a, 25b, 26c
Si	28a, 29b, 30c
S	32a, 33c, 34b
Cl	35a, 37b
A	36b, 38c, 40a
K	39a, 40c, 41b
Ca	40a, 42c, 43d, 44b, 46f, 48e
Ti	46b, 47c, 48a, 49d, 50e
Cr	50c, 52a, 53b, 54d
Fe	54b, 56a, 57c, 58d
Co	59a, 57b

* *Note:* The letters a, b, c, d, etc. indicate the relative quantities, in decreasing order, of the various atoms in the naturally occurring element.

TABLE 6—(*contd.*)

Mass Numbers of Isotopes

Element	Masses of Isotopes
Ni	58a, 60b, 62c, 64e
Cu	63a, 65b
Zn	64a, 66b, 67d, 68c, 70e
Ga	69a, 71b
Ge	70c, 72b, 73d, 74a, 76e
Se	74f, 76c, 77e, 78b, 80a, 82d
Br	79a, 81a
Kr	78f, 80e, 82c, 83d, 84a, 86b
Rb	85a, 87b
Sr	84d, 86b, 87c, 88a
Zr	90a, 91d, 92b, 94c, 96e
Mo	92d, 94e, 95c, 96b, 97g, 98a, 100f
Ru	96a, (98), 99f, 100d, 101b, 102a, 104c
Rh	101b, 103a
Pd	102f, 104e, 105c, 106a, 108b, 110d
Ag	107a, 109b
Cd	106g, 108h, 110c, 111e, 112b, 113d, 114a, 116f
In	113b, 115a
Sn	112h, 114i, 115j, 116c, 117e, 118b, 119d, 120a, 122g, 124f
Sb	121a, 123b
Te	122f, 123g, 124e, 125d, 126c, 128b, 130a
Xe	124h, 126h, 128g, 129a, 130f, 131c, 132b, 134d, 136e
Ba	130f, 132g, 134e, 135d, 136c, 137b, 138a
Ce	140a, 142b
Nd	142a, 143d, 144b, 145e, 146c, 148f, 150g
Sa	144g, 147c, 148e, 149d, 150f, 152a, 154b
Eu	151a, 153a
Gd	152f, 154c, 155b, 156a, 157c, 158a, 160d
Dy	158e, 160d, 161c, 162b, 163b, 164a
Er	162f, 164e, 166a, 167c, 168b, 170d
Yb	168g, 170f, 171e, 172b, 173c, 174a, 176d
Lu	175a, 176b
Hf	174f, 176e, 177c, 178b, 179d, 180a
W	180e, 182c, 183d, 184a, 186b
Re	185a, 187a
Os	184g, 186e, 187f, 188d, 189c, 190b, 192a
Ir	191b, 193a
Pt	192e, 194b, 195a, 196c, 198d
Hg	196g, 197h, 198e, 199c, 200b, 201d, 202a, 203i, 204f
Tl	203b, 205a
Pb	204d, 206b, 207c, 208a
U	234c, 235b, 238a

* *Note:* The letters a, b, c, d, etc. indicate the relative quantities, in decreasing order, of the various atoms in the naturally occurring element.

Hydrogen as prepared by chemical methods consists of two isotopes, $^{1}_{1}H$ and $^{2}_{1}H$ known respectively as protium and deuterium. The proportion of deuterium in ordinary hydrogen is very small (i.e. 1 part in 4500). The deuterium atom possesses one electron but its nucleus consists of one proton and one neutron. Deuterium oxide is often termed "heavy water" and deuterium "heavy hydrogen," the nucleus of the deuterium atom is known as the *deuteron*. A summary of the chief physical properties of the isotopes of hydrogen and their oxides is given in Table 7.

TABLE 7

Chief Physical Properties of the Isotopes of Hydrogen and Their Oxides

Property of Isotopes	Hydrogen	Deuterium
Boiling point . . .	20·38°A	23·50°A
Triple point . . .	13·92°A	18·58°A
Heat of fusion . . .	28 cal/mol	47 cal/mol
Property of Oxides	**Hydrogen oxide (Water, H_2O)**	**Deuterium oxide (Heavy water, D_2O)**
Density at 25°C . .	1·0	1·1079
Boiling point . . .	100·0°C	101·42°C
Freezing point . . .	0·0°C	3·82°C
Surface tension . . .	72·75 dynes/cm	67·8 dynes/cm

Isobares. From Table 6 it will be noted that there are several instances of isotopes of different elements having the same atomic weight (e.g. argon, potassium and calcium, and titanium and chromium). These isotopic forms having the same atomic weight are known as *isobares*.

Packing Fraction. It has been stated previously that the α-particle is a helium atom carrying two positive charges. It therefore consists of two protons and two neutrons. Since the mass of a proton is 1·00758 mass units, and that of a neutron 1·00893 mass units, the mass of the nucleus of the helium atom should be $(2 \times 1{\cdot}00758) + (2 \times 1{\cdot}00893)$ mass units $= 4{\cdot}03302$ mass units.

In actual fact the mass of the helium atom nucleus is 4·0028 mass units. This difference of approximately 0·030 mass units, termed the *mass defect* represents the "binding energy" of the protons and neutrons in the nucleus of the helium atom.

By the employment of the Einstein equation,

$$E = mc^2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

it can be shown that this extremely small amount of mass is equal to $4{\cdot}5 \times 10^{-5}$ ergs per nucleus, or $2{\cdot}7 \times 10^{19}$ ergs per gramme molecule of helium. Expressed in other units, this means that to break up all the nuclei in one gramme atom of helium would require energy equivalent to $1{\cdot}62 \times 10^{11}$ gramme calories, or 190 000 kilowatt hours of electrical energy. And, of course, conversely, if free protons and free neutrons could be built into helium nuclei this amount of energy would be released. In a similar way, atoms heavier than helium are of less mass than they would be if formed by the union of protons and neutrons without change in mass.

This decrease in mass is usually defined by the so-called *packing fraction* which is evaluated as follows—

$$\text{Packing fraction} = \frac{\text{Isotopic atomic weight} - \text{Mass number}}{\text{Mass number}} \times 10^4 \quad . \quad (9)$$

A negative packing fraction indicates that the isotopic atomic weight is less than integral and that mass has been converted into energy in the formation of that particular nucleus. Such nuclei are particularly stable. On the other hand, a positive value for the packing fraction, in general, indicates instability of the nucleus, except for elements of small atomic weight.

The lowest packing fractions are exhibited by the transition elements lying between chromium and zinc (*see* Fig. 17), in the first long period of the Periodic Table, and these elements, therefore, are regarded as the most stable of all the elements since if any one of these elements were to be converted into another element, the total mass of elements produced would be slightly greater than that of the elements serving as reactants, and accordingly, bearing in mind Einstein's equation, a tremendous amount of energy would have to be supplied to bring about such a change. As the mass number increases, the packing fraction increases until, with mass numbers exceeding approximately 200, it becomes positive, this fact agreeing with the occurrence of radioactivity by such elements.

The Extra-nuclear Electrons. So far consideration of the extra-nuclear electrons has been confined to the statements that their number is determined by the atomic number (i.e. the number of positive charges in the nucleus), and that they constitute a relatively "transparent" structure surrounding the nucleus. The arrangement of the extra-nuclear electrons in successive shells according to well-established laws is, however, of considerable importance.

Information regarding the arrangement of the electrons may be obtained from optical spectra and from X-ray spectra; the former arise from disturbances in the outer part of the electronic structure and the latter from electronic disturbances close to the nucleus. In the formation of chemical compounds minor re-arrangements occur of the outermost electrons.

In the nuclear theory of the atom as proposed by Lord Rutherford, it was necessary to assume a very rapid planetary movement of the electrons around the nucleus so that the attractive force inwards was exactly counterbalanced by the outward centrifugal force. This reasoning, however, is unsound and the parallel between the solar system and the nuclear atom untrue since the sun and the planets are not electrically charged, whereas the nucleus and the extra-nuclear electrons have definite electric charges. According to electromagnetic theory an electron should emit radiation

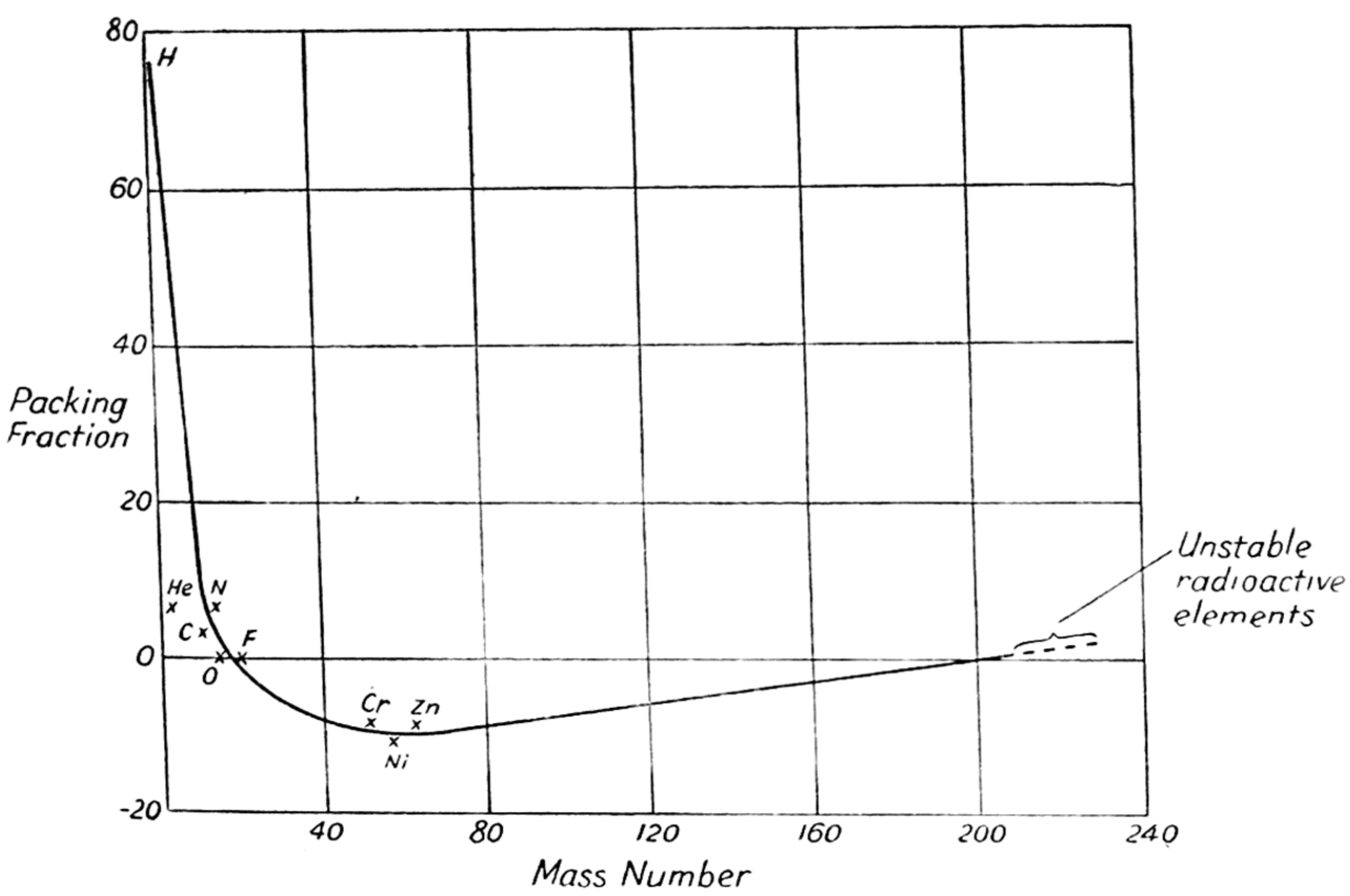


FIG. 17. Packing Fractions of the Elements

continuously during its circulation and, therefore, the radius of curvature of its path will progressively decrease in the form of a spiral so that eventually the electron will fall into the nucleus.

It was to overcome these difficulties that Niels Bohr in 1913 put forward a theory which combined Lord Rutherford's theory of the nuclear atom with Planck's Quantum Theory. The resulting atomic model is usually known as the "Rutherford-Bohr atom." According to Planck's Quantum Theory, radiation is only capable of being emitted or absorbed in units of energy, or *quanta*,

$$\varepsilon = h\nu \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where ε = a quantum of energy, h = a universal constant, known as *Planck's constant*, ν = the frequency of the radiation.

In his application of the Quantum Theory, Bohr suggested that an electron always rotated around the nucleus in a closed orbital, and so long as this type of motion occurs there is no absorption or emission of radiation. Bohr postulated that for any electron more than one stable orbital was possible, each orbital being known as an "energy level."

Since the angular momentum of a particle such as an electron moving in a circular orbital is

$$\omega = mvr \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where ω = angular momentum, m = mass of electron, v = speed of rotating electron, r = radius of orbital, then, by the application of wave mechanics, it can be shown that the possible electronic orbitals are defined by the expression—

$$mvr = n\frac{h}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where n = an integer termed the *Quantum Number* of the particular energy level, h = Planck's constant.

From (12) it will be noted that as the radius of the electronic orbital, r, increases so does the numerical value of the quantum number, and thus the quantum number may be regarded as indicating the order of the various orbitals commencing with that nearest to the nucleus and counting outwards. Thus, for the first possible orbital, $n = 1$, for the second, $n = 2$, and so on. Bohr also stated that when an electron jumps from one orbital to another with a lower energy level, the surplus energy is emitted as radiation of a specific frequency (that is, a definite spectral line). Since a number of different energy levels are possible in every atom there will therefore be a number of simultaneous transitions of electrons, and hence a series of lines will be apparent in the *line spectrum*. On the other hand, when atoms of an element are in a condition of excitation such as obtains by the employment of a high temperature or an electrical discharge, then the electrons will absorb energy and in doing so pass from lower energy levels to higher energy levels (i.e. from inner orbitals to outer orbitals). These changes in energy levels give rise to the production of *absorption lines* in *absorption spectra*, each absorption line corresponding to a specific electronic transition from a lower to a higher energy level.

From the study of line spectra it has been shown that elements with similar spectra are also similar chemically. In fact, the spectrum of an element may be regarded as a periodic property, and it is from the study of line spectra in particular that most of the present detailed knowledge of the extra-nuclear structure of the atom has been obtained.

The atom of hydrogen was originally thought to consist of a single proton with a single electron moving in a circular orbital, but it is now known that the electron travels in an elliptical orbital, and instead of rotating in one plane it travels in all directions, thus describing in its

rotation a spherically symmetrical shell. In this way, by virtue of its rapid speed (i.e. $2{\cdot}18 \times 10^8$ cm/sec, or approximately 1 per cent of the speed of light) it effectively occupies all the space within a radius of approximately 1 Å of the nucleus. Thus, a free hydrogen atom may be said to consist of a sphere of effective diameter of approximately 2 Å at the centre of which is a proton comprising the nucleus whilst the intervening space is occupied by a very rapidly moving electron.

After hydrogen, the next heavier element is helium which possesses two electrons, each of which rotate around the nucleus in a similar manner to the single electron in the hydrogen atom. These two electrons are said to occupy the *K* shell which may be occupied by not more than two electrons. All atoms heavier than helium possess two electrons in the *K* shell and in addition possess extra-nuclear electrons arranged in concentric electron shells external to the *K* shell. The successive shells are distinguished by the names *L*, *M*, *N*, *O* and *P* shells respectively. These shells are also designated by the numbers 1, 2, 3, 4, 5 and 6, the values for the quantum numbers used in the mathematical description of electronic motion in terms of quantum theory.

Helium is one of a group of elements termed the "inert gases" (also known as the "rare gases," or "noble gases") which are outstanding as their name suggests by virtue of their being chemically inert. This pronounced lack of chemical reactivity implies a very great atomic stability as is emphasized by the fact that the *ionization energy* is greater for the inert gases than for the atoms of other elements. Ionization energy is the energy required to remove an electron from the atom, or in other words the energy absorbed by the reaction

$$X \rightarrow X^+ + e^-$$

In a similar way the energy liberated on picking up an additional electron (i.e. the *electron affinity*) as depicted by the reaction

$$X + e^- \rightarrow X^-$$

is zero for the inert gases. The atomic numbers of the inert gas group are given below, in addition to helium.

Inert Gas	Atomic Number
Helium	2
Neon	10
Argon	18
Krypton	36
Xenon	54
Radon	86

The atom of neon consists of two electrons in the *K* shell and eight electrons in the *L* shell. Argon in addition to having two electrons in the *K* shell and eight electrons in the *L* shell also has an additional eight electrons in the *M* shell. In the case of the next heavier inert gas, krypton, there are eight electrons in the outer *N* shell but in the next inner shell, that is the *M* shell, the eight electrons as existent in argon have increased to eighteen. In the case of xenon there is a new outer shell of eight electrons in the O shell, but again the next inner shell, that is, the *N* shell, has expanded from eight electrons to eighteen electrons. With radon there are eight electrons in the *P* shell but here the number of electrons in the *N* shell has increased to thirty-two, whilst in the *O* shell the number of electrons as present in xenon has increased from eight to eighteen.

The successive electronic shells, *K*, *L*, *M*, *N*, *O* and *P* have electronic structures as shown in Table 8.

TABLE 8

Electronic Configuration of the Inert Gases

Inert Gas	Atomic Radius (Å)	Atomic Number	Number of Electrons in Quantum Levels					
			1(*K*)	2(*L*)	3(*M*)	4(*N*)	5(*O*)	6(*P*)
Helium . .	0·9	2	2					
Neon . . .	1·1	10	2	8				
Argon . . .	1·5	18	2	8	8			
Krypton . .	1·7	36	2	8	18	8		
Xenon . .	1·9	54	2	8	18	18	8	
Radon . .	2·2	86	2	8	18	32	18	8

The addition of successive outer electron shells does not greatly increase the size of atoms of elements such as the inert gases just described, since as the atomic number increases, the corresponding shells of electrons decrease in size so permitting a new outer shell to be only a little larger than that of the shell which it envelopes.

It is therefore possible to assign so-called "atomic radii" or "ionic radii" to atoms and ions. The atomic radii of the inert gases are given in Table 8.

Electron Subshells. From a detailed study of line spectra using spectroscopes of high resolving power it was found that a spectral line, which appeared single at low resolution, exhibited a fine structure consisting of two or more lines close together. The existence of this fine structure is explained by assuming that certain of the electrons travel in elliptical orbitals, although the maximum number of separate orbitals, that is circular and elliptical orbitals, for each principal quantum level is equal to the number of that quantum level.

Thus, in reporting quantum numbers it is usual to denote the principal or original quantum number by the letter *n* and the degree of ellipticity by the letter *l*. The numerical values of *n* and *l* in accordance with the above statement are as follows—

n (Principal Quantum Number)	*l* (Degree of Ellipticity of Orbital)
1	0
2	0 or 1
3	0, 1 or 2
4	0, 1, 2 or 3
and so on	

The numerical values for the degree of ellipticity are denoted by letters, *s* for 0, *p* for 1, *d* for 2, and *f* for 3, and the number of electrons possessing the same quantum number indicated by a superscript. Thus, for example $4f^{14}$ denotes 14 electrons each with $n = 4$ and $f = 3$.

In order to explain all the observed characteristics of line spectra it is necessary to specify quantum numbers in addition to the two described above. For example, a third quantum number, the *magnetic quantum number* denoted by the symbol *m*, takes into account the effects of magnetic and electric fields in splitting spectral lines; whilst a fourth, the *spin quantum number*, denoted by the symbol *s*, indicates the influence on spectral lines of direction of spin of the electron (i.e. whether clockwise or anti-clockwise) on its axis. Considerable assistance in connexion with the problem of electronic arrangement in atoms has been provided by the Pauli "Exclusion Principle" which states that any orbital can contain up to two electrons, but no more; if it contains two they must have opposite spins.

Except for special purposes, however, it is sufficient—at least as far as a study of chemistry is concerned—to quote the values of *n* and of *l* for each electron.

Electronic Structure of the Elements

The maximum number of electrons existing in the shells increases as twice the square of the numbers, 1, 2, 3 and 4—the principal quantum numbers of the first four quantum levels—as shown below—

$$2(1^2) = 2$$
$$2(2^2) = 8$$
$$2(3^2) = 18$$
$$2(4^2) = 32$$

Since the atomic number of an atom is equal to the number of extra-nuclear electrons, and further since the atomic numbers of the inert gases, 2, 10, 18, 36, 54 and 86, represent the completion of successive electron shells, Langmuir deduced that the number of electrons in each shell may be evaluated by subtracting from the total number of electrons in any inert gas atom the number of electrons in the preceding inert gas. This gives 2, 8, 8, 18, 18 and 32 for the numbers of electrons in the successive complete electron groups.

These numbers are, it will have been noted, the numbers of elements in the successive periods of the Periodic Table (*see* p. 40), so that each period represents a progressive completion of an electron shell in passing from an alkali metal to an inert gas, and in each period, after the first, the maximum number of electrons in the main group is repeated once before proceeding to the next higher number in the general series, i.e. $2(1^2)$, $2(2^2)$, $2(2)^2$, $2(3^2)$, $2(3)^2$, and $2(4^2)$. This is often known as the *Rydberg series*, since Ryberg (1914) first pointed out its significance.

First Period. The atom of hydrogen consists of a nucleus composed of a proton and a single electron circulating in the *K* shell or 1-quantum level—that is, one 1*s* electron.

The atom of helium which consists of a nucleus with a net positive charge of two, possesses two extra-nuclear electrons. Since these two electrons represent a full complement for the *K* shell, helium is a very stable element exhibiting no tendency in the ordinary chemical sense to lose, or acquire or share electrons. In fact, according to the usual nomenclature, helium is classified as an inert gas.

Second Period. In contradistinction to the *K* shell or 1-quantum level, which may not hold more than two electrons, the *L* shell or 2-quantum level is capable of holding from one to eight electrons. Thus, with the elements of atomic numbers from 3 to 10 (i.e. lithium to neon) constituting the first short period of the Periodic Table, the electrons in the *L* shell increase from one to eight. This is indicated below using the "electron-dot" notation. It should be noted that with the object of effecting simplification the two inner electrons of the *K* shell are omitted.

Li Be . B . . C . : N . : O . : F . : Ne :

In the *L* shell there are four orbitals, one 2*s* orbital and three 2*p* orbitals, each capable of occupation either by a single electron or two electrons. Two such electrons travelling in a single orbital constitute an *electron pair*.

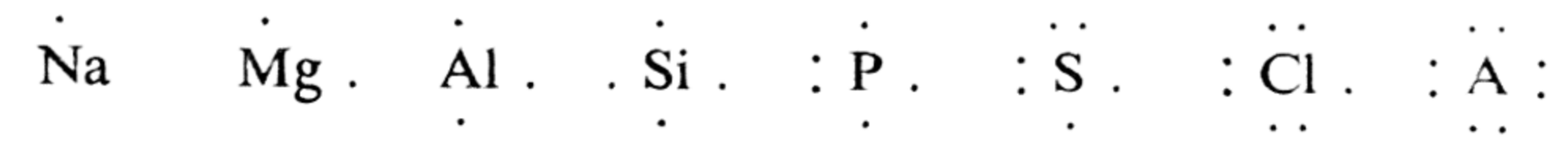
In this period carbon possesses four unpaired electrons, one in each of the four orbitals. On the other hand, neon makes four electron pairs of its eight *L* electrons. This completed inert gas outer shell of four electron pairs is known as an "octet" of electrons. For a more complete picture of the electronic configuration of some of the simpler atoms, reference should

be made to Table 9; particular attention should be paid to the orbitals in which the electrons rotate.

Third Period. This quantum level, the second short period of the Periodic Table commences with the alkali metal, sodium and finishes with the inert gas, argon.

In the 3-quantum level or the *M* shell there are four orbitals, one 3*s* orbital and three 3*p* orbitals.

The elements in this period have an increasing number of electrons as indicated diagrammatically below.



Fourth Period. This period consists of the eighteen elements which constitute the first long period of the Periodic Table. These eighteen elements fall into two divisions, two elements falling in each of the Groups I to VII of the Periodic Table, three elements—iron, cobalt and nickel—occurring in Group VIII, and one element, krypton being found in Group O.

This period commences with potassium which possesses a single 4*s* electron circulating around the "argon core"; calcium, the next element, has two 4*s* electrons; but with scandium, titanium and vanadium a new electronic arrangement obtains since these three elements all possess two 4*s* electrons, but in addition have one, two and three electrons respectively at the 3-quantum level, i.e. 3*d*.

Chromium and manganese, the elements with the next highest atomic numbers, have five 3*d* electrons, but whereas chromium has one 4*s* electron, manganese has two 4*s* electrons.

The elements iron, cobalt and nickel each retain two 4*s* electrons, but also have six, seven and eight 3*d* electrons respectively. These electronic structures are detailed in Table 9.

The elements copper to krypton all have the same "copper core" as shown in Table 9, but whereas copper has a single 4*s* electron the remaining seven elements, zinc, gallium, germanium, arsenic, selenium, bromine and krypton all possess two 4*s* electrons, and in addition, the final six elements possess successively one up to six 4*p* electrons (*see* Table 9).

Fifth Period. The electronic arrangement of the 5-quantum level of some of the elements composing the second long period of the Periodic Table is shown below.

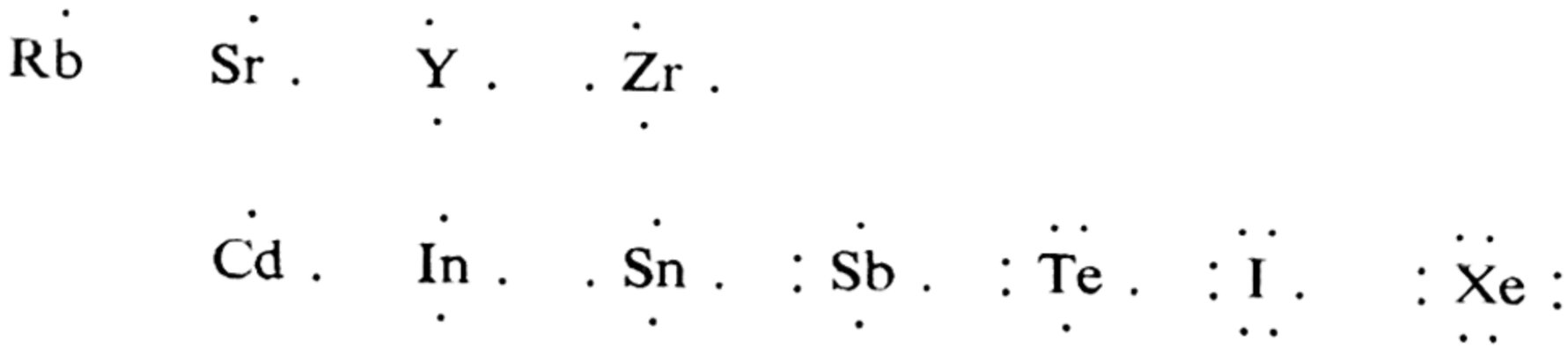


TABLE 9

Electronic Structures for Elements in the First Four Periods of the Periodic Classification

		Shell									
		K	L		M			N			
Element	Atomic No.	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
H	1	1									
He	2	2									
Li	3	2	1								
Be	4	2	2								
B	5	2	2	1							
C	6	2	2	2							
N	7	2	2	3							
O	8	2	2	4							
F	9	2	2	5							
Ne	10	2	2	6							
Na	11	Neon Core			1						
Mg	12				2						
Al	13	2	2	6	2	1					
Si	14				2	2					
P	15				2	3					
S	16				2	4					
Cl	17				2	5					
A	18				2	6					
K	19	Argon Core						1			
Ca	20							2			
Sc	21						1	2			
Ti	22	2	2	6	2	6	2	2			
V	23						3	2			
Cr	24						5	1			
Mn	25						5	2			
Fe	26						6	2			
Co	27						7	2			
Ni	28						8	2			
Cu	29	Copper Core						1			
Zn	30							2			
Ga	31	2	2	6	2	6	10	2	1		
Ge	32							2	2		
As	33							2	3		
Se	34							2	4		
Br	35							2	5		
Kr	36							2	6		

Addition of electrons at the fifth quantum level does not exclude further additions of electrons at the fourth quantum level and it is important to note that a number of electrons, once attained at a given quantum level, is not always maintained.

Sixth Period. In the case of this period, which commences with the element caesium the first addition of an electron is at the 6-quantum level, but subsequent additions of electrons both at the 4- and 5-quantum levels occur.

The first three elements in this period are caesium, barium and lanthanum. To the next fourteen elements the title *rare earth metals* has been given. With the exception of the 4*f* orbitals all these rare earth metals have the same number of electrons in all the quantum levels up through 6*s* and 6*p* orbitals. Into the seven 4*f* orbitals there are successively introduced, one at a time, fourteen electrons. This, no doubt, is at least part of the explanation for the chemical similarity of the rare earth metals since chemical behaviour is largely determined by the number of electrons in the outermost quantum level.

CHAPTER 4

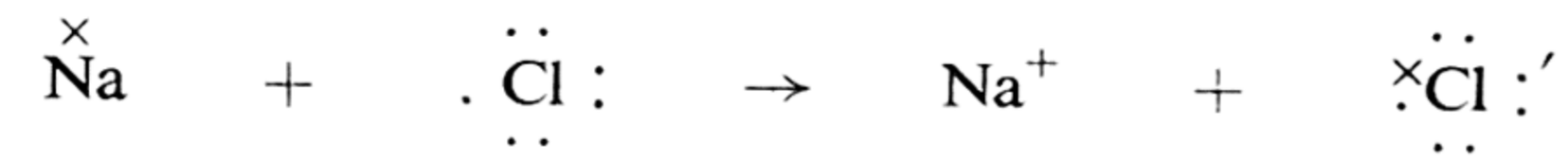
THE ELECTRONIC THEORY OF VALENCY

THE concept of valency has already been introduced in a general and somewhat empirical manner (*see* p. 12). In this connexion the configuration of the extra-nuclear electrons described earlier is of some very considerable value in making possible a more precise explanation of valency from the electronic standpoint, and accordingly it will be from this standpoint that valency is discussed in the present chapter.

In the formation of molecules and chemical compounds, three types of bonding or linkage are possible, namely the electrovalent bond, the covalent bond, and the co-ordinate link (or dative bond).

THE ELECTROVALENT BOND

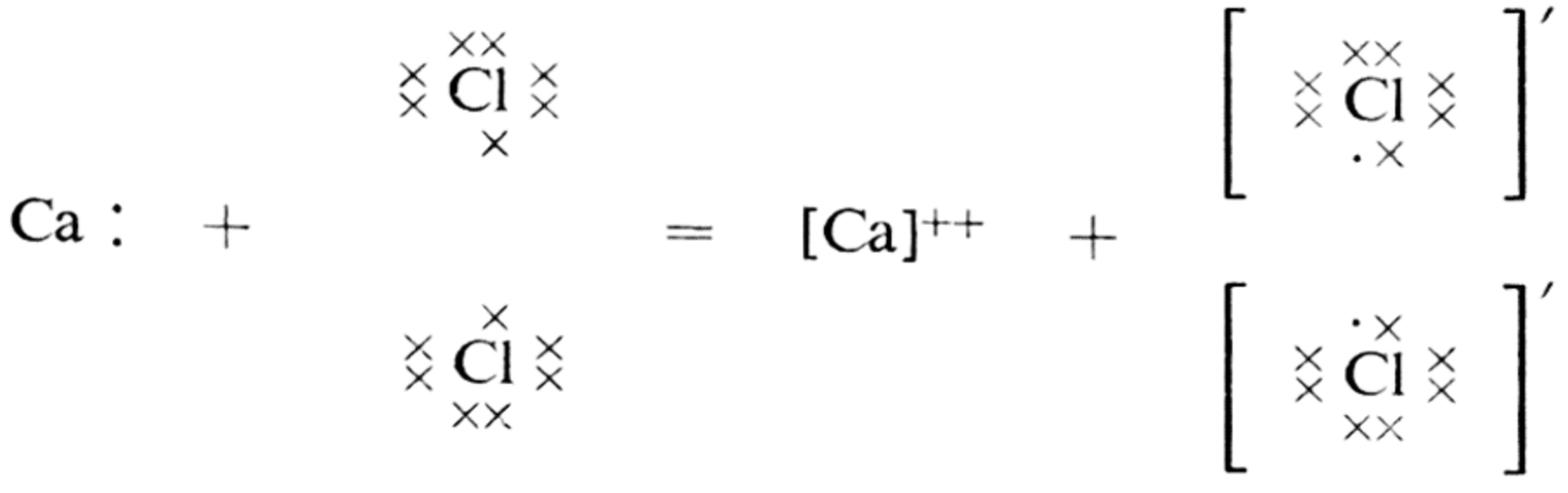
The electrovalent bond is also known variously as the ionic bond, polar bond, electronic bond, and heteropolar bond. Its essential feature is the transfer of electrons from one atom to another. This may be illustrated by reference to the formation of sodium chloride from its component elements, thus—



In the reaction quoted above, the electrically neutral sodium atom has transferred the single electron in its outermost shell to the chlorine atom, which already has seven electrons in its outermost shell, so as to allow of the chlorine atom completing its octet. Both types of atoms now have eight electrons in their outermost orbits and so have attained the stability of an inert gas. Since the sodium has lost unit negative charge (i.e. an electron) the residue exhibits a positive charge; in fact it is the sodium *ion*. In a similar manner, since the chlorine atom has gained an electron it therefore exhibits a negative charge and constitutes what is known as the chlorine *ion*. In the solid state a crystal of sodium chloride consists of a three-dimensional assembly of equal numbers of sodium and chlorine ions and the stability of these ions, as illustrated by their inert nature when sodium chloride dissolves in water, and when the salt is melted or even boiled so as to convert the material into the vapour state, may be attributed to the attainment of the inert gas structure by the two ions under consideration.

When fused sodium chloride or an aqueous solution of this salt is electrolyzed the sodium ion migrates to the cathode (i.e. the negative pole) during electrolysis and is therefore termed a *cation*. The negatively-charged chlorine ion migrates to the anode (i.e. the positive pole) during electrolysis and is known as the *anion*.

Similarly, the atoms of the elements in Group II of the Periodic Table, having two electrons in their outermost shells or quantum levels, can lose these electrons to form bipositive ions (e.g. Mg^{++}, Ba^{++}, Ca^{++}), and likewise certain elements in Group III form terpositive ions (e.g. Al^{+++}). Thus, ionic compounds are formed between some of the strongly metallic elements which occur in Groups I, II and III of the Periodic Table and the non-metals at the extreme right of the Periodic Table. This is further exemplified by the formation of calcium chloride and calcium sulphide.



In addition, however, the formation of ionic compounds also occurs between the cations of the strongly metallic elements and the anions of acids, particularly oxygen acids. The chief oxygen acids and their corresponding anions are given in Table 10.

TABLE 10

The Chief Oxygen Acids and their Anions

Name of Acid	Formula	Name of Anion	Formula
Nitric acid	HNO_3	Nitrate	NO_3'
Chloric acid	$HClO_3$	Chlorate	ClO_3'
Perchloric acid	$HClO_4$	Perchlorate	ClO_4'
Sulphuric acid	H_2SO_4	Sulphate	SO_4''
Sulphurous acid	H_3SO_3	Sulphite	SO_3''
Carbonic acid	H_2CO_3	Carbonate	CO_3''
Phosphoric acid	H_3PO_4	Phosphate	PO_4'''
Silicic acid	H_4SiO_4	Silicate	SiO_4''''

The ease of ion formation bears some relation to the size of the atom. In the case of small atoms, electrons from the outermost shell are the only ones undergoing transfer, but in the case of heavier atoms the shell underneath the outermost shell may also lose electrons; e.g. in the formation of the Cr^{+++} ion, two electrons are taken from the outermost shell and one electron from the shell immediately underneath. Such metals therefore form ions which do not possess the inert gas structure. It should be noted however that as the number of electrons in the outermost shell increases, greater difficulty is experienced in effecting electron transfer; in fact, the tendency is to gain electrons to attain a stable octet like the inert gases. This is, of course, most pronounced in the case of the halogens.

From the foregoing discussion it will be noted that a substance is a metal, or exhibits metallic properties when it forms positive ions by loss of valency electrons. The characteristics of the electrovalent bond may be enumerated as follows—

(1) In the electrovalent bond the ions are held together by electrostatic forces.

(2) Although in electrovalent compounds no definite structural bond exists, the presence of the strong electrostatic field makes it more difficult to separate molecules of electrovalent compounds than those of covalent compounds with the result that electrovalent compounds are solids whose melting points and boiling points in the great majority of cases are higher than those of covalent compounds. Thus, for example, the solid, sodium chloride, a typical electrovalent compound has a boiling point of 1490°C whilst the boiling point of the liquid covalent compound, carbon tetrachloride is 76°C.

(3) Electrovalent compounds are usually soluble in abnormal liquids like water, in which they dissociate into individual ions. Electrovalent compounds do not readily dissolve, however, in normal liquids such as the covalent liquids ether and benzene.

THE COVALENT BOND

The essential feature of the covalent bond, also known as the homopolar bond, is the sharing of electrons *without* the formation of ions.

In the formation of covalent bonds two important points should be noted, namely—

(i) the sharing of electrons in pairs, each electron pair or "duplet" being equivalent to one conventional chemical bond, and

(ii) the acquisition by each atom of eight electrons—an "electron octet"—in its outermost shell, which thus corresponds to the electronic structure of one of the inert gases. Hydrogen is an exception to this general statement since it acquires the structure of helium for which only two electrons are necessary.

The Hydrogen Molecule. The simplest example of the covalent bond is

provided by the hydrogen molecule for which the electronic structure may be shown as $H^{\times}_{\cdot}H$ which indicates that the two electrons are shared by the two hydrogen atoms making up the hydrogen molecule. The very great strength of this bond is shown by the fact that in order to separate the two individual atoms in a single hydrogen molecule a very considerable amount of energy is required (i.e. 103·4 k.cal/mol*). A hydrogen atom can therefore attain the stable electronic structure of the inert gas helium by sharing an electron pair (a duplet) with another hydrogen atom, the shared pair being counted first for one atom and then for the other.

The Halogen Molecules. The halogens possess an electronic configuration in which there are seven electrons in their outermost shells (or quantum levels) and lacking only one electron in order to attain the structure of an inert gas. This structure may be attained by one halogen atom forming a single covalent bond with another halogen atom and it is this bond which holds together the diatomic halogen molecules in the solid, liquid and gaseous states.

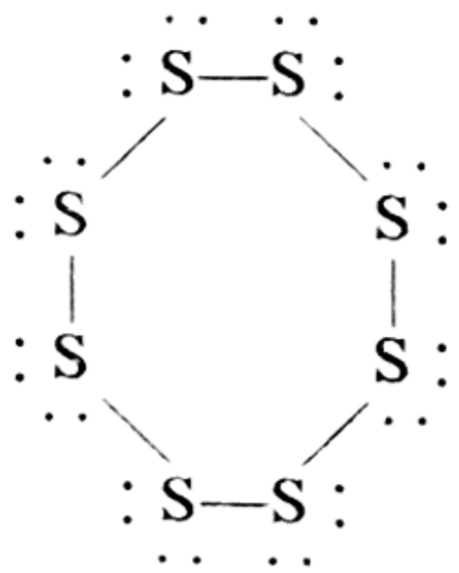
In the "electron-dot" notation these bonds may be depicted as follows—

$$:\dot{\underset{\cdot\cdot}{F}}\times\dot{\underset{\times\times}{F}}: \quad \text{or} \quad :F-F: \qquad\qquad :\dot{\underset{\cdot\cdot}{Cl}}\times\dot{\underset{\times\times}{Cl}}: \quad \text{or} \quad :Cl-Cl:$$

$$:\dot{\underset{\cdot\cdot}{Br}}\times\dot{\underset{\times\times}{Br}}: \quad \text{or} \quad :Br-Br: \qquad\qquad :\dot{\underset{\cdot\cdot}{I}}\times\dot{\underset{\times\times}{I}}: \quad \text{or} \quad :I-I:$$

Sulphur and Elements of Group VI. An atom of sulphur requires two electrons to complete its octet. This may be done by one sulphur atom forming single covalent bonds with two other sulphur atoms, so holding together the atoms either in a ring of eight sulphur atoms, *see* (*A*) below, forming the S_8 molecule, or alternatively in the form of a long chain of large numbers of sulphur atoms, *see* (*B*), p. 72. The so-called "plastic sulphur" is composed of sulphur atoms in the long chain type of structure, whilst other forms of sulphur are composed of S_8 molecules.

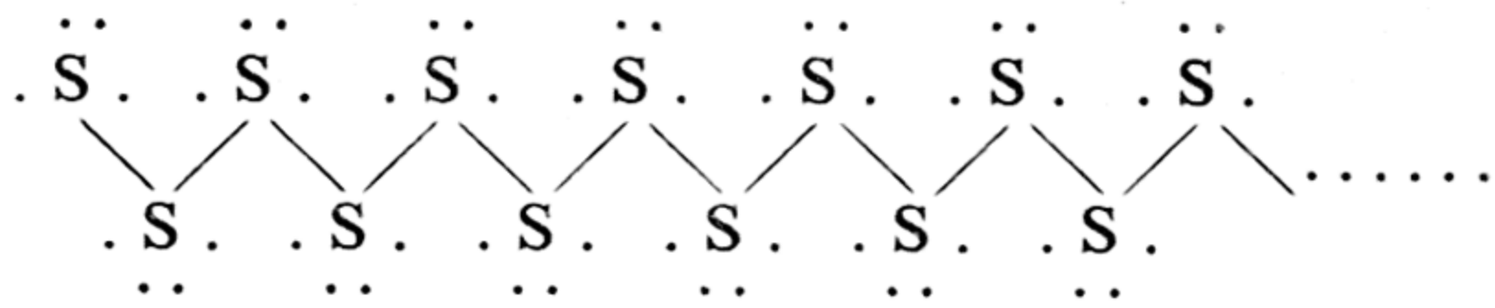
(*A*)



* Compare this value with 57·8 k. cal/mol, the energy liberated when molecular hydrogen is oxidized to water according to the equation—

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \text{ (gas)}$$

(*B*)



In a similar manner, the element selenium crystallizes either as red crystals made up of Se_8 molecules, or as grey crystals built up of crystals containing long chains similar to those occurring in plastic sulphur. Likewise, in tellurium crystals there is also present the long chain type of crystal structure.

Gaseous oxygen is composed of diatomic molecules and it might be thought that in order to complete the octet for each atom, two electron pairs would be shared between the two atoms, in other words a *double bond* might be present, thus, $:\dot{\underset{\cdot\cdot}{O}}::\dot{\underset{\cdot\cdot}{O}}:$ or $:\dot{\underset{\cdot\cdot}{O}}=\dot{\underset{\cdot\cdot}{O}}:$, but this is not the case. Instead, only one pair of electrons is shared between the two atoms, leaving two unpaired electrons as follows—

$$:\dot{\underset{\cdot\cdot}{O}}:\dot{\underset{\cdot}{O}}: \quad \text{or} \quad :\dot{\underset{\cdot\cdot}{O}}—\dot{\underset{\cdot}{O}}:$$

Nitrogen and Elements of Group V. The nitrogen atom requires three electrons to complete its octet and this is attained by the formation of three covalent bonds, three electron pairs being shared by two nitrogen atoms, thus—

$$:N:::N: \quad \text{or} \quad :N\equiv N:$$

This bond is a very strong one and the nitrogen molecule is correspondingly a stable molecule.

The phosphorus molecule is composed of four atoms each forming covalent bonds with its three partners, the molecule itself having a tetrahedral structure.

Carbon and Elements of Group IV. The atom of carbon, with its deficit of four electrons necessary for completion of its octet, can attain the inert gas structure by forming four covalent bonds. This it does in the diamond in which each atom is linked to four neighbouring atoms sited at the corners of a regular tetrahedron (*see* Fig. 18), and since these bonds are very strong, this assembly of atoms constitutes a hard substance. It is well known that the diamond is the hardest substance known to man.

On the other hand the atoms of carbon in graphite are arranged in a structure in which each atom has three near neighbours being bonded to two by single covalent bonds and to the third by a double covalent bond, as in Fig. 19.

The tetrahedral arrangement of the four carbon atoms in the diamond to which reference has just been made is not merely a coincidence but is the

expression of an important property exhibited by the octet, namely that the four electron pairs, whether shared or not, tend to arrange themselves in space at the corners of a regular tetrahedron. Silicon, germanium and grey tin also crystallize with the diamond structure. White tin and lead have metallic structures.

Summarizing the foregoing facts, in the formation of covalent bonds the structures possessed by stable molecules are such that each atom attains the electronic structure of an inert gas, or some other stable electronic configuration, the shared electrons being counted for each of the atoms involved in the bond.

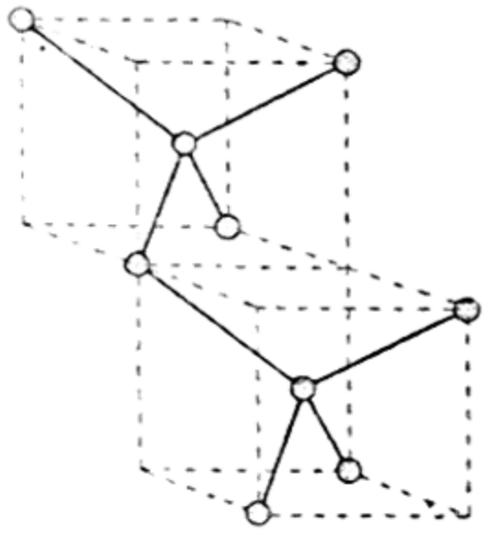


FIG. 18. The Tetrahedral Arrangement of Carbon Atoms in the Diamond

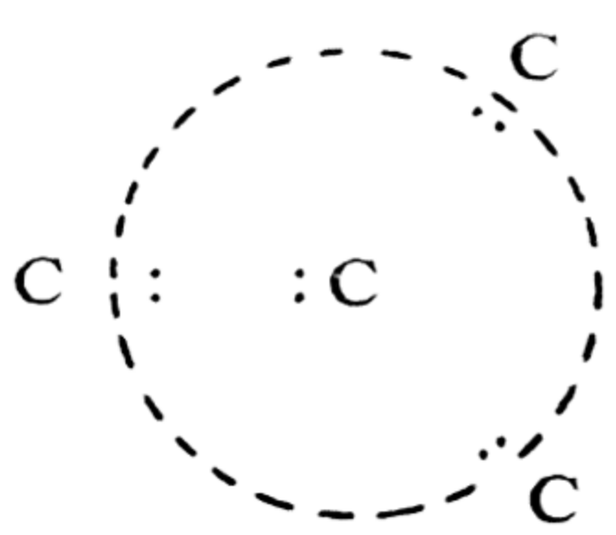
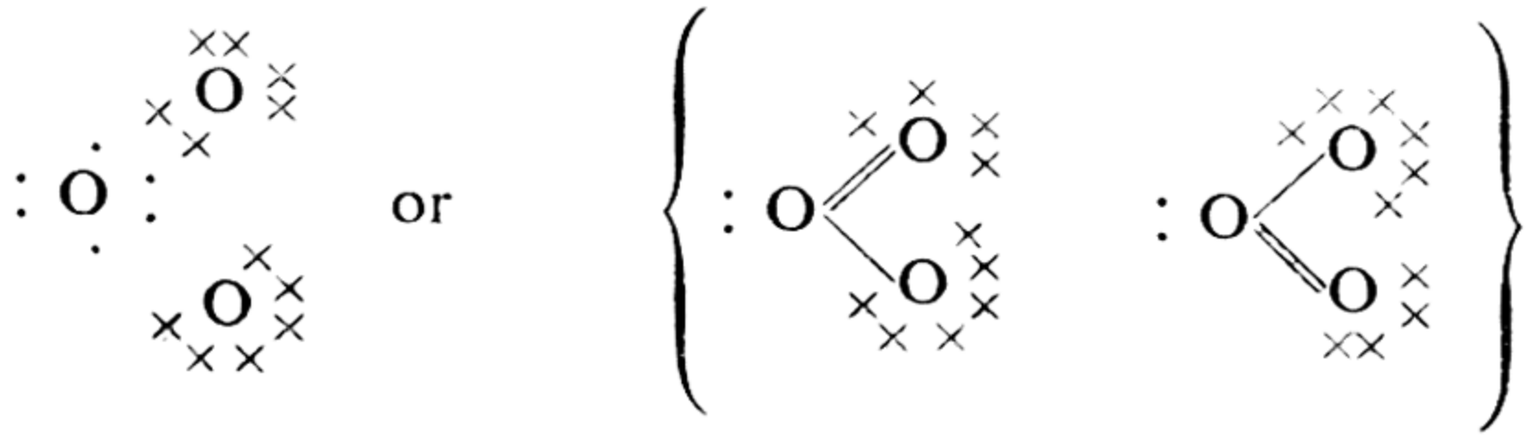


FIG. 19. Arrangement of Carbon Atoms in Graphite

Resonance (or Mesomerism)

From the electronic structure of ozone (*see* below) it will be noted that one of the end atoms completes its octet by sharing only one electron pair, whilst the central oxygen atom forms three covalent bonds—one double bond and one single bond. From experimental considerations, however, it is known that these two oxygen bonds in ozone are not different but are equivalent, and this is explained by the assumption of a *hybrid* structure. In other words, each of the covalent bonds in ozone is a hybrid between a single bond and a double bond so that its properties are of intermediate character. In this connexion it is usual to state that in ozone the double bond "resonates" between the two positions.

When writing structural formulae in such cases as ozone the various electronic structures are written within brackets, thus—

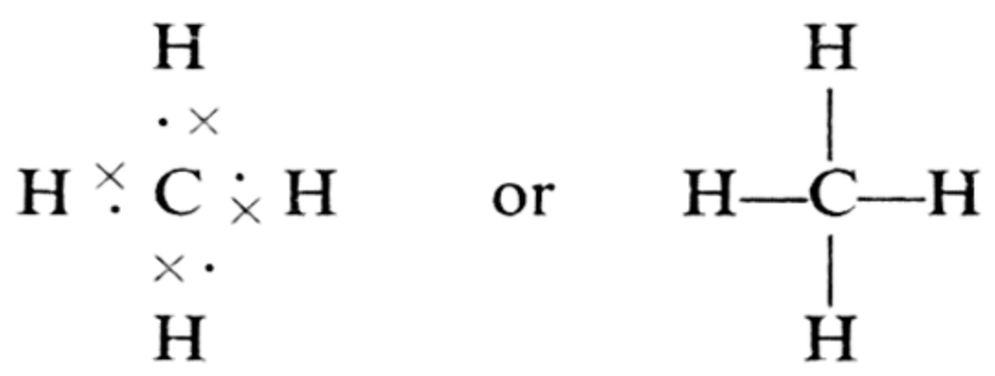


so indicating that the electronic structure is a hybrid structure of two or more structures.

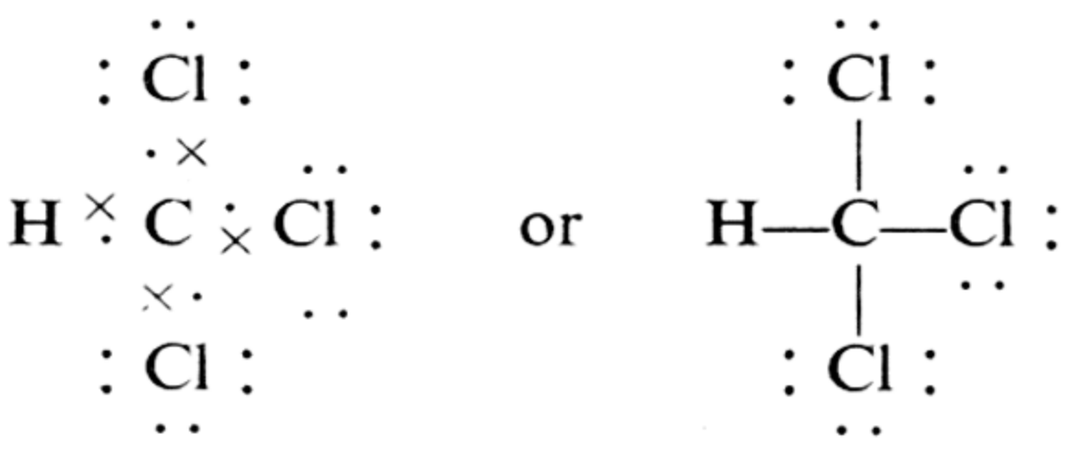
The phenomenon of resonance is also displayed in chemical compounds as well as in elemental structures.

The Electronic Structure of Covalent Compounds and Radicals

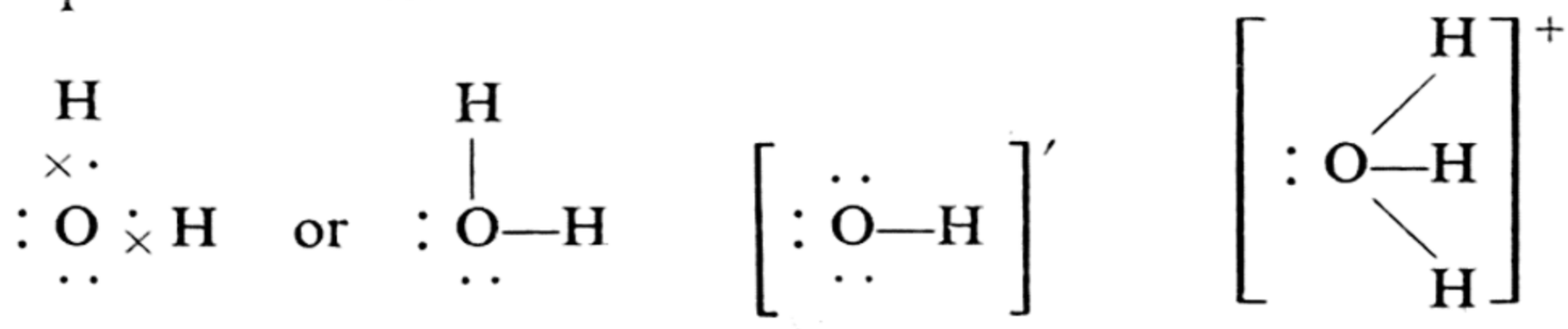
As well as forming molecules containing the same atoms, atoms may combine to form covalent compounds; methane, CH_4, may be depicted by the following tetrahedral covalent structural formula—



and similarly, chloroform, $CHCl_3$, as follows—



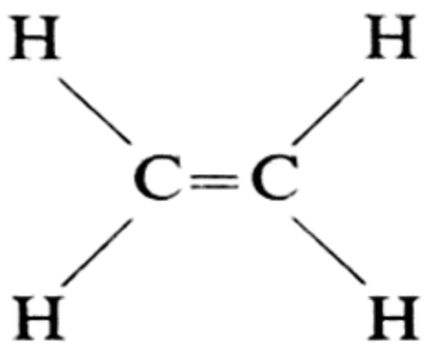
Although these molecules are depicted in the two dimensions of the printed page, it is important to appreciate that in actual fact the octet electrons assume the tetrahedral form, and therefore a three-dimensional model is requisite for complete description. Other examples of molecular structures are shown below. It will be noted that whilst resonating structures are enclosed within "curly" brackets, complex ions are enclosed within square brackets.



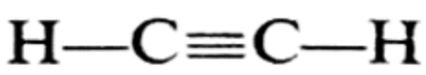
Water

Hydroxyl ion occurring in basic solutions

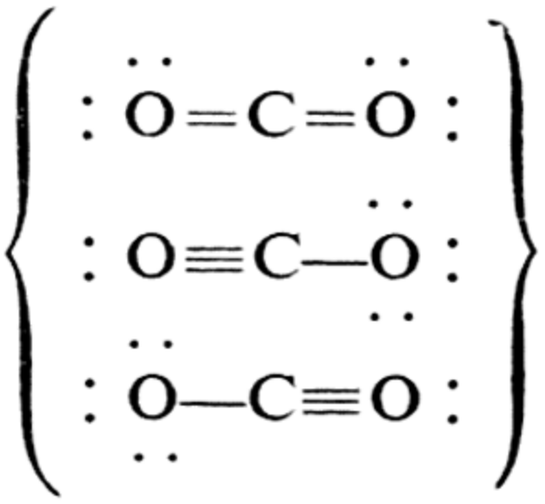
Hydroxonium ion occurring in acid solutions



Ethylene



Acetylene (Linear molecule)



Carbon dioxide (Linear molecule)

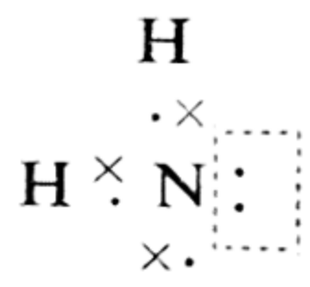
From the examples quoted above the general characteristics of the covalent bond may be enumerated as follows—

(i) The covalent bond is rigid and directional so that the molecules have a definite shape. Thus atoms of the molecule can neither part company, nor change their positions within the molecule without the molecule undergoing chemical decomposition. Covalent bonds are much stronger than electrovalent bonds.

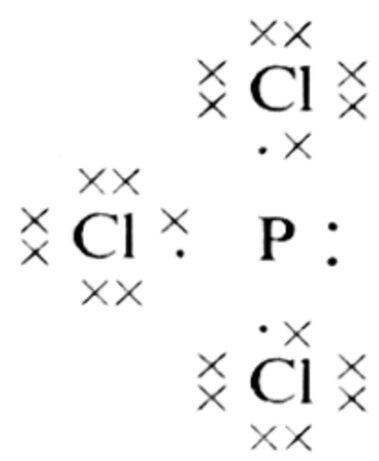
(ii) Since in the formation of covalent bonds all the atoms retain their electrical neutrality, the molecule exhibits little external field of force, and covalent compounds, therefore, are either gases, or alternatively solids or liquids which are capable of easy volatilization. In general, covalent compounds exhibit lower melting points and boiling points than electrovalent compounds.

(iii) Covalent compounds are usually only slightly soluble in abnormal liquids such as water which cause dissociation; they are however soluble in normal liquids (e.g. ether, benzene). Covalent compounds are non-electrolytes.

The structural formula for the gaseous compound, ammonia, is—



from which it will be noted that two electrons in the octet for nitrogen are unshared with the hydrogen atoms; such an unshared pair (shown within the dotted line) is termed a "lone pair." Similarly, there also exists a lone pair in phosphorus trichloride as shown below.

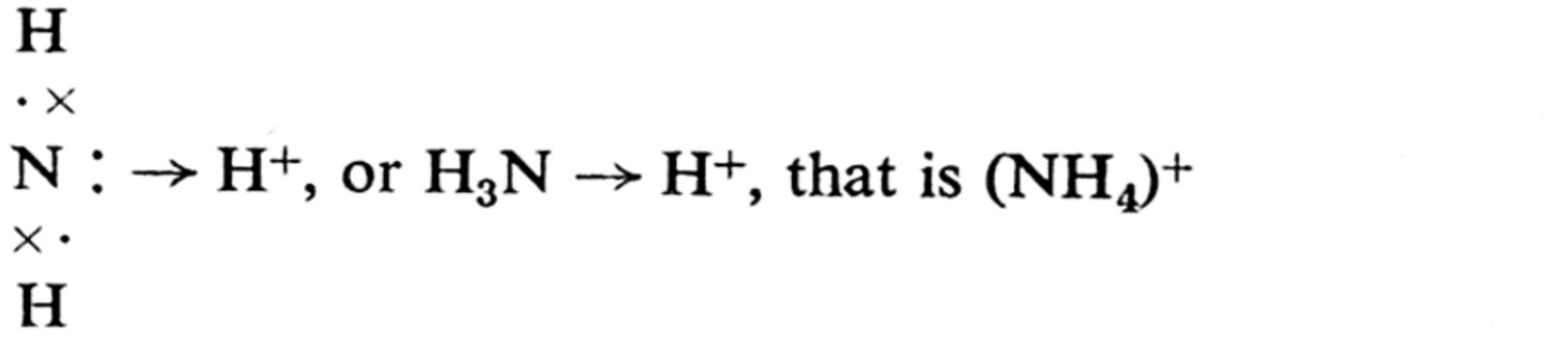


THE CO-ORDINATE LINK

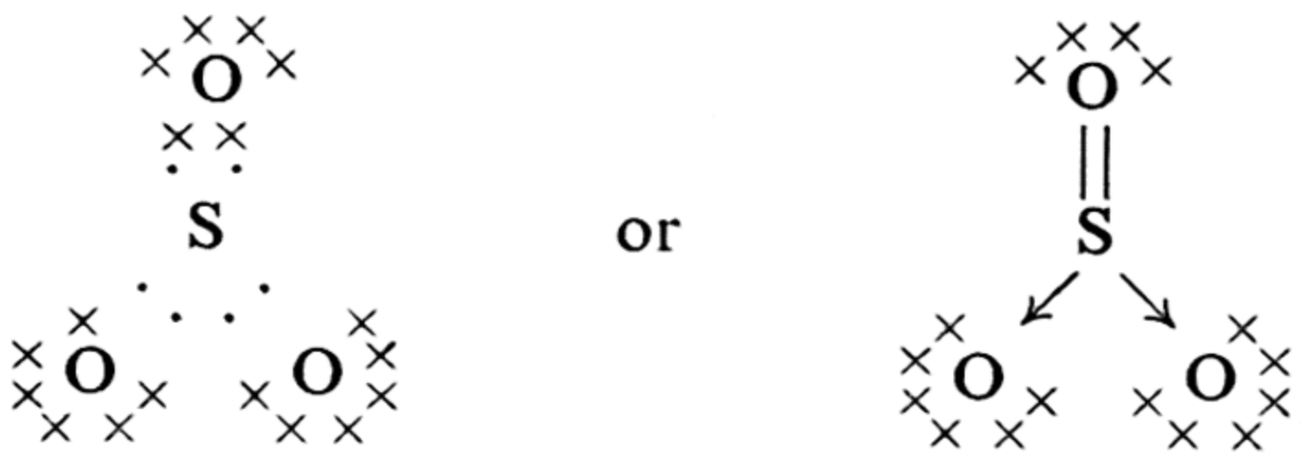
The co-ordinate link, known variously as dative covalency, the dative bond, and the semi-polar bond, is a variety of the covalent bond in which both electrons constituting the duplet are supplied by one atom, the terms "donor" and "acceptor" being employed to describe the two atoms or molecules involved in a dative bond. Thus, atoms or molecules with lone pairs are donors, whilst those atoms or molecules which do not contribute electrons to the bond are acceptors. An arrow is often used in structural

formulae to indicate in which direction donation of the electron pair has proceeded.

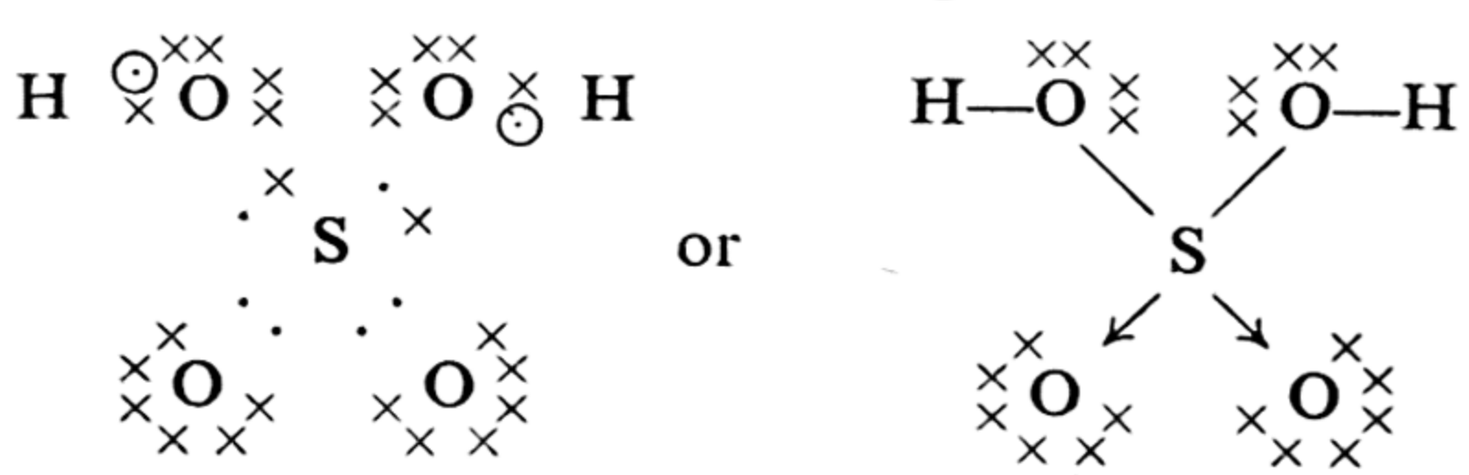
In the formation of the ammonium ion from the ammonia molecule and a hydrogen ion, the nitrogen atom acts as donor of an electron pair to the hydrogen ion, as follows—



Another example is provided by sulphur trioxide which has the structural formula



The double bond between the central sulphur atom and the oxygen atom is unstable, but on reaction with water, to form sulphuric acid, this double bond is replaced by two single bonds with increased stability as indicated by the large quantity of heat liberated during this reaction.



Electrons from hydrogen atoms shown thus, ⊙.

In aqueous solution the two hydrogen atoms ionize, leaving behind the divalent sulphate radical on which there now reside two negative charges since the two electrons, previously part of the two hydrogen atoms, have been left as part of the radical on the hydrogen atoms becoming hydrogen ions. The formation of sulphuric acid by the chemical union of sulphur trioxide and water thus provides an example of an acid with a covalent

structure whose metallic salts are ionic in character. The structures of other oxygen acids (*see* Table 10, p. 69) are capable of description in a similar manner to that given above.

Distinction between Electrovalent and Covalent Compounds

The readiness with which metals form ions is chiefly determined by two factors—

(*a*) The number of electrons in the outermost shell (the valency electrons) of the metal atom.

(*b*) The atomic volume of the metal.

The higher the valency of a metal, the greater will be the number of electrons in the outermost shell. Now, since the positive charge resident upon the nucleus remains unaffected by the removal of electrons, its attractive effect will progressively increase with the removal of each successive electron. It follows that when there are a number of electrons in the outermost shell, the removal of electrons will become progressively more and more difficult with the loss of each successive electron.

The larger the atomic volume of an atom, the less strongly will the positively-charged nucleus be able to hold the electrons in the outermost shell (i.e. the valency shell); in other words, the more readily will such an atom lose one or more electrons to become an ion. Such is the case with the atoms of a large number of metals.

Although it is possible, by the loss of several electrons, for certain metal atoms to form polyvalent cations up to a maximum valency of four (e.g. tin forms the tetravalent stannic ion, Sn^{++++}), the formation of polyvalent anions is extremely difficult since for the acquisition of each additional electron the attractive force exerted by the nucleus on each individual electron becomes progressively smaller. It is for this reason that the maximum valency for a simple anion is found to be two.

Employing considerations such as those discussed above, Fajans has related the occurrence of the electrovalent and the covalent bonds to the position of an element in the Periodic Table. Fajans has suggested that with decreasing size and increasing charge of the positive ion, and with increasing size of the negative ion, there is an increasing tendency for a compound to be covalent rather than electrovalent. Expressed in another way, the various conditions tending to give rise to either electrovalent bonds or to covalent bonds in compounds are as follows—

Electrovalent Bond Favoured by	Covalent Bond Favoured by
Large atomic volume of cation	Small atomic volume of cation
Small atomic volume of anion	Large atomic volume of anion
Small charge on either ion	Large charge on either ion

Influence of Solvation upon Nature of Chemical Bonding

The chemical properties of covalent compounds in the pure state are often very different from the chemical properties of the same substance in solution. These differences are due to the effect of *solvation*. For example, pure hydrogen chloride is a covalent compound, but in aqueous solution it suffers *hydration* (i.e. solvation by water) and behaves as a compound with pronounced electrovalent characteristics, the two ions present being the hydrated hydrogen ion, that is the hydroxonium ion, H_3O^+, and the chloride ion, Cl'. The change from covalent to electrovalent characteristics is no doubt due to the increase in the size of the cation by virtue of its hydration.

Pure sulphuric acid is also a covalent compound, but in aqueous solution the two hydrogen atoms present in each molecule of sulphuric acid suffer hydration and become hydroxonium ions with the result that electrolytic dissociation occurs and the solution contains hydroxonium ions and sulphate ions.

THE ELECTRONEGATIVITY SCALE

The power of attraction of atoms for electrons in a covalent bond is termed the *electronegativity* of the element. From the observed heats of formation of compounds the electronegativity scale has been drawn up as shown in Table 11. This electronegativity scale is of value in determining the type of bonding existent in chemical compounds.

In general, the greater the quantity of heat evolved in a chemical reaction, the greater the strength of the chemical bond established. This may be illustrated by reference to the heats of formation of the hydrogen halides as follows—

$$H_2 + F_2 \rightarrow 2HF + 128 \text{ k.cal}$$
$$H_2 + Cl_2 \rightarrow 2HCl + 44{\cdot}12 \text{ k.cal}$$
$$H_2 + Br_2(g) \rightarrow 2HBr + 24{\cdot}95 \text{ k.cal}$$
$$H_2 + I_2(g) \rightarrow 2HI + 3{\cdot}09 \text{ k.cal}$$

Thus the greater the separation of two elements on the electronegativity scale, the greater is the strength of the bond between them. If two elements are separated by 1·7, the bond possesses approximately 50 per cent electrovalent character. If the separation is greater than 1·7 the electrovalent structure should be used for the compound, whilst conversely, for numerical values less than 1·7 the employment of the covalent structure would seem to be more appropriate.

The Partial Ionic Character of the Covalent Bond

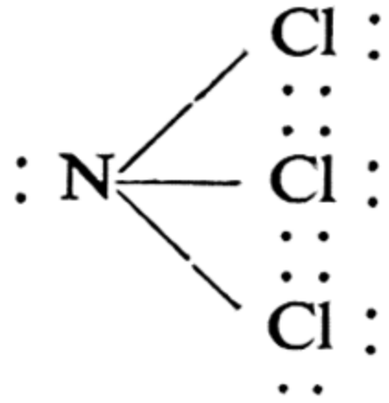
It is sometimes difficult in the case of a compound to decide whether the bonding is due to electrovalent bonds or to covalent bonds. For example, in the case of the first short period of the Periodic Table, the first five

TABLE 11

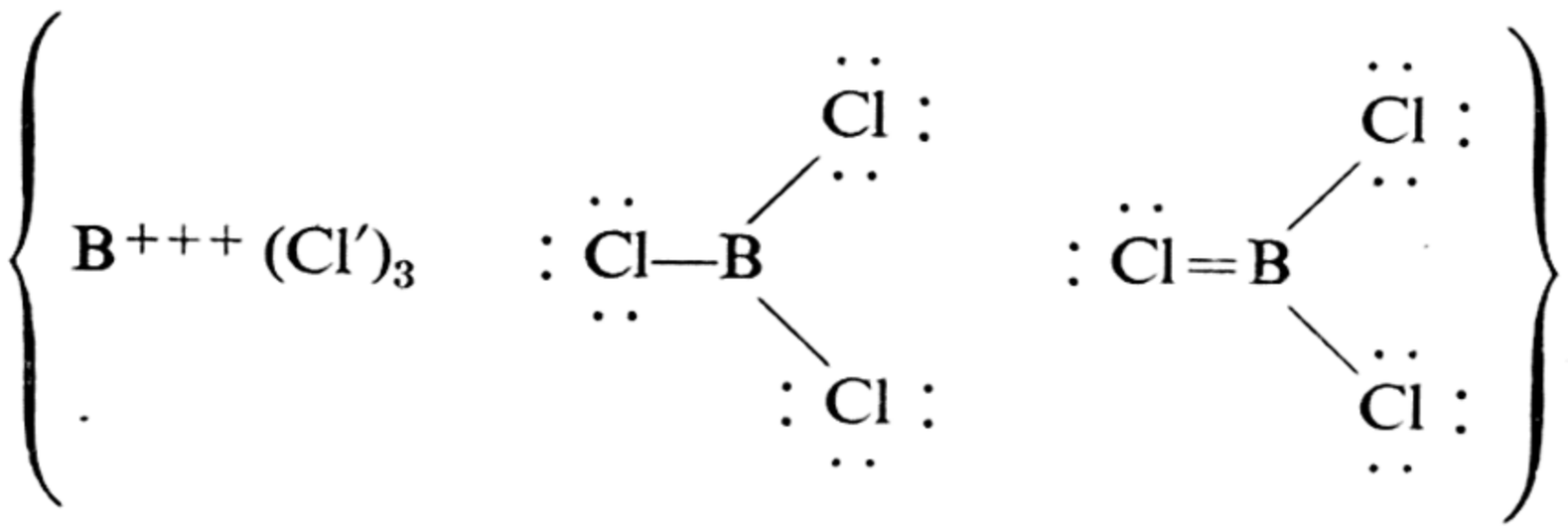
Electronegativity Values for Selected Elements

Group in Periodic Table	Element	Electronegativity Value
1	Hydrogen	2·1
	Lithium	1·0
	Sodium	0·9
	Potassium	0·8
	Rubidium	0·8
	Caesium	0·7
II	Beryllium	1·5
	Magnesium	1·2
	Calcium	1·0
	Strontium	1·0
	Barium	0·9
III	Boron	2·0
	Aluminium	1·5
	Scandium	1·3
	Ytterbium	1·3
IV	Carbon	2·5
	Silicon	1·8
	Titanium	1·6
	Zirconium	1·6
	Germanium	1·7
	Tin	1·7
V	Nitrogen	3·0
	Phosphorus	2·1
	Arsenic	2·0
	Antimony	1·8
VI	Oxygen	3·5
	Sulphur	2·5
	Selenium	2·4
	Tellurium	2·1
VII	Fluorine	4·0
	Chlorine	3·0
	Bromine	2·8
	Iodine	2·4

elements are lithium, beryllium, boron, carbon and nitrogen. The salt, lithium chloride, LiCl, formed from a strongly metallic element and a strongly non-metallic element is clearly, in the light of the previous discussion, an electrovalent compound containing the two ions Li^+ and Cl'. On the other hand, the oily compound nitrogen trichloride, NCl_3, most definitely possesses the covalent structure



But between these two compounds there exist the three chlorides beryllium chloride, $BeCl_2$, boron trichloride, BCl_3, and carbon tetrachloride, CCl_4, and the question arises as to when the electrovalent bonding ceases and covalent bonding commences. In actual fact the transition from the normal electrovalent bond to the normal covalent bond is a gradual one and although beryllium chloride and carbon tetrachloride are electrovalent and covalent compounds respectively, and may therefore be represented as such, the structure of the boron trichloride molecule is best represented as a resonating structure, thus—



Thus, in boron trichloride, although covalent bonds may be shown, they exhibit, to some extent at least, ionic characteristics. Such bonds are often termed "covalent bonds with partial ionic character."

The Covalency Maximum

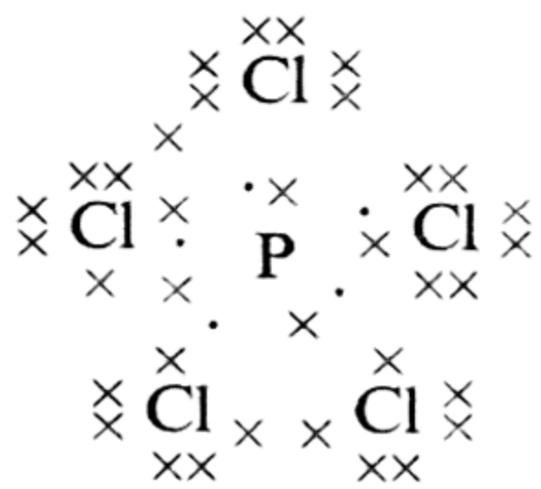
Although the "Octet Rule" holds in the case of elements of low atomic weight in that the maximum number of electrons capable of existence in the outermost electron shell is limited to eight, this is not the case as one proceeds to elements of higher atomic weight found later in the Periodic Table. If the essential feature of a covalency bond is to be retained, namely the sharing of electrons in pairs or duplets, then it is necessary to expand the valency group.

Thus, if the structnre of phosphorus pentachloride is depicted as a

covalent compound, the central phosphorus atom is surrounded by ten electrons, as shown at (*A*).

Similarly, in sulphur hexafluoride, the central sulphur atom is surrounded by twelve electrons (*B*). Sidgwick has suggested that the maximum number of covalencies which the elements may exhibit are as shown in Table 12 (*see* below).

(*A*)



(*B*)

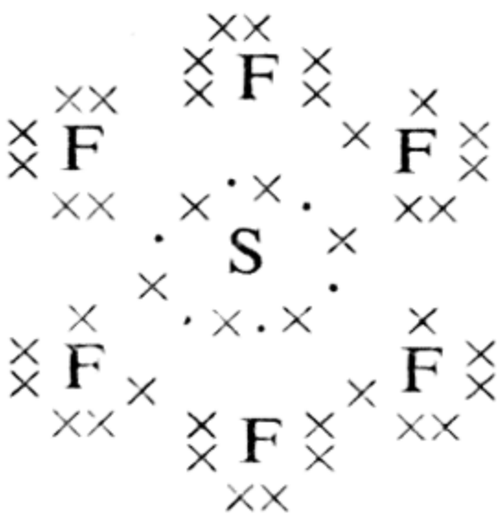


TABLE 12

Maximum Covalencies of the Elements

Elements in Order of Increasing Atomic Weight	Maximum Number of Covalencies
Hydrogen	1
Lithium to fluorine . .	4
Sodium to yttrium . . .	6
Zirconium to uranium . .	8 (With possibly ten in the heavier elements)

CO-ORDINATION COMPOUNDS

In depicting the structure of many complexes it is necessary to assume an increase in the number of covalency bonds if the existence of the duplet is to be assumed. In this connexion it has been shown that there is a tendency

for certain atoms to link themselves to a definite number of other atoms, radicals or groups, irrespective of their valency; the maximum number of

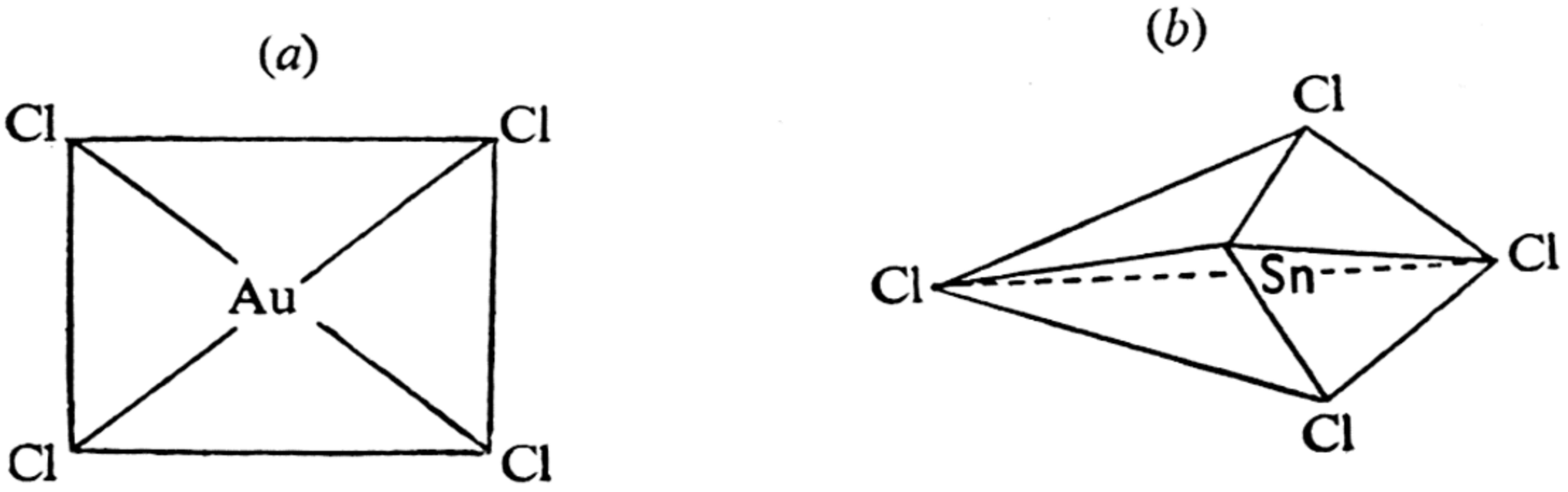


FIG. 20. (*a*) Planar and (*b*) Tetrahedral Structure of 4-co-ordinated Compounds

groups which may thus be added being known as the "co-ordination number"; usually this is four or six, so that one speaks of 4-co-ordination and 6-co-ordination compounds. For example, in the case of the ferrocyanide ion, the element iron exhibits 6-co-ordination. The ferrous ion

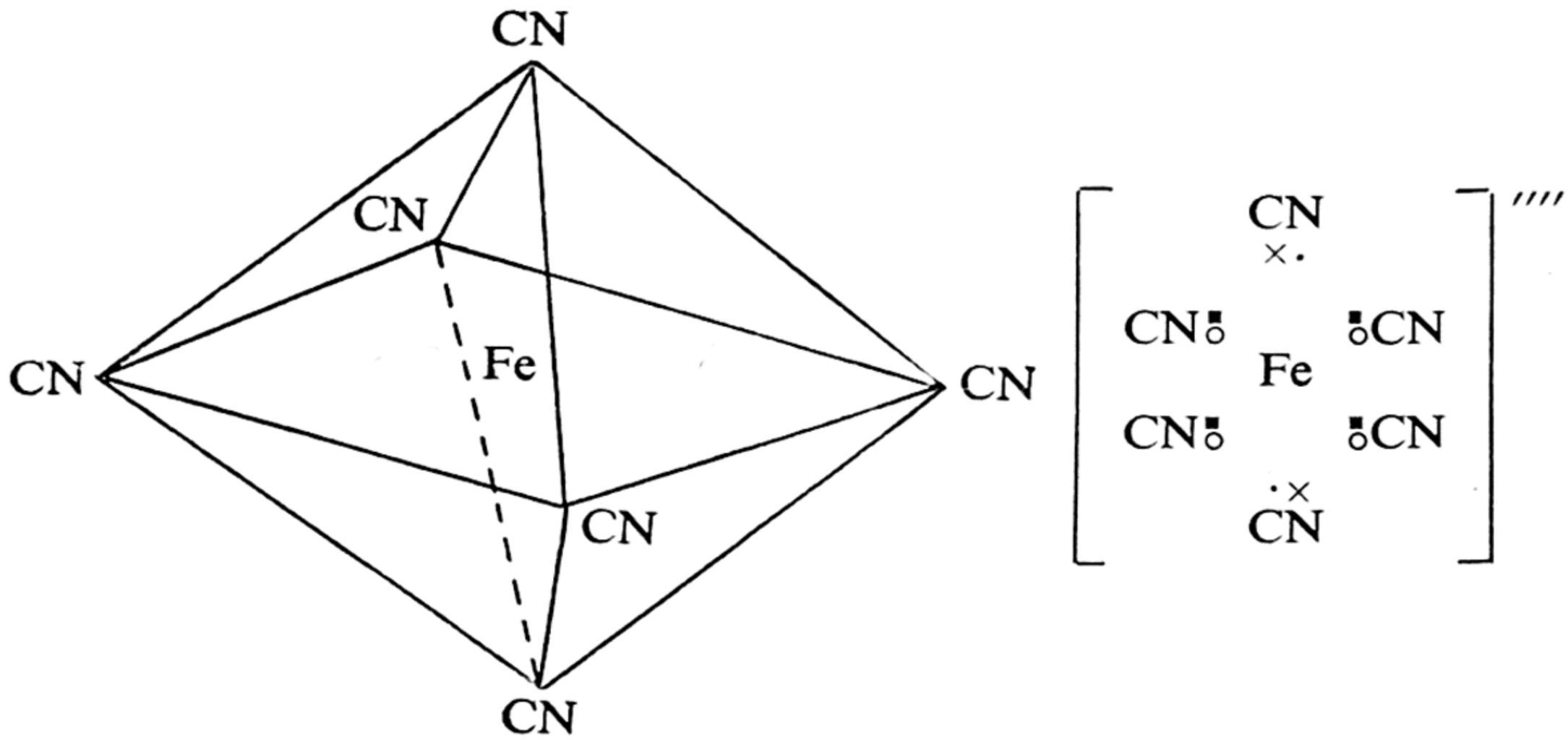


FIG. 21. Structure of Ferrocyanide Ion

has two electrons of its own, represented by crosses (in Fig. 21), which, with the two electrons (represented by dots) from two cyanide radicals (say from potassium cyanide), form two covalent bonds. In addition, four further cyanide radicals are taken up by the central iron atom (from potassium cyanide as before), but since each of these radicals possesses only one electron (represented by squares), four extra electrons (represented by open circles) must be transferred at the same time from the four

potassium atoms involved in the reaction to form the co-ordination complex. These last four bonds are dative bonds.

The structures of many complexes have been investigated by Werner who has shown that 4-co-ordinated complexes may exhibit either a planar or a tetrahedral structure (*see* Fig. 20), whilst 6-co-ordinated complexes must be octahedral as shown in the case of the ferrocyanide ion (*see* Fig. 21).

By means of such structures Werner has been able to demonstrate the existence of isomers. For example, there are two complexes to which the following formula may be given, $[Co(NH_3)_4Cl_2]^+$; one isomer is green in colour whilst the other is violet. These two structures are shown below (*see* Fig. 22).

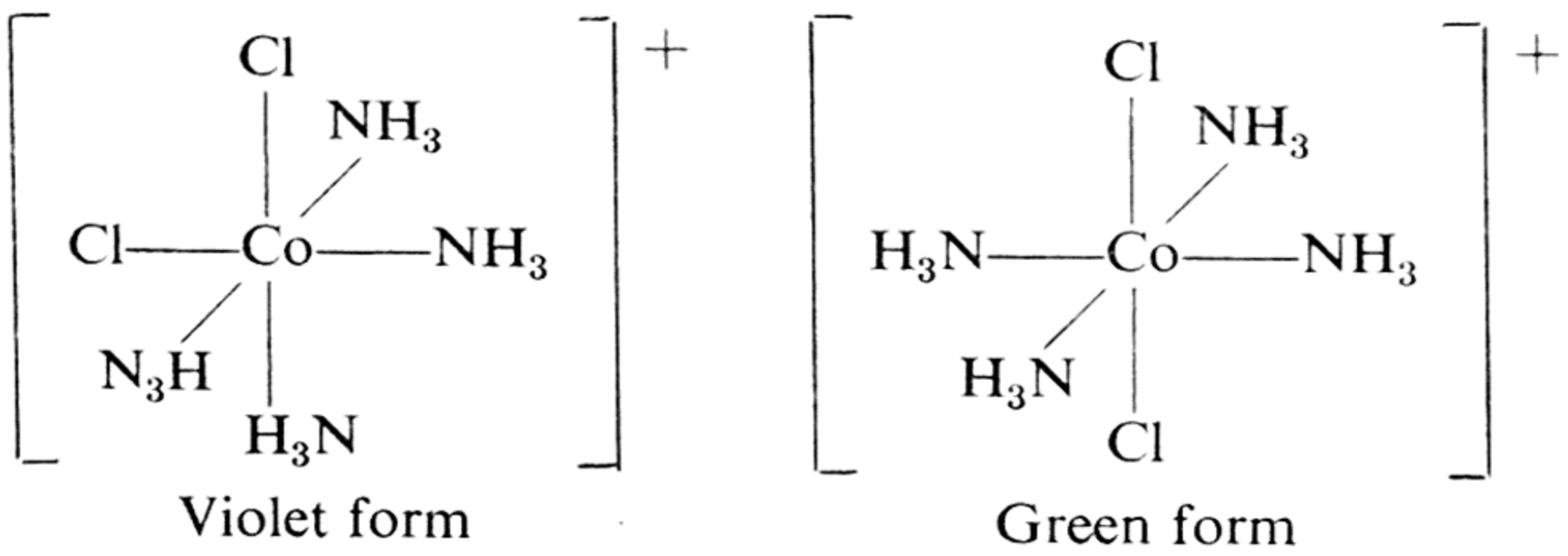


FIG. 22. Violet and Green Forms of Cobaltammine Compound

CHAPTER 5

THE GASEOUS STATE

A GAS is characterized by its marked sensitivity to undergo a change of volume should its temperature or pressure be varied, and also by the fact that it possesses no boundary surface, as do liquids and solids, with the result that it tends to fill completely any space within which it is confined.

THE KINETIC THEORY OF GASES

Many of the characteristics of gases, such as those mentioned above, suggest that gases are composed of molecules in a state of rapid motion. This motion accounts for the absorption of heat by the gas. Gaseous molecules are free to move about and for the most part do not exert any appreciable influence upon their neighbours. It is well known that the increase of pressure leads to a reduction in the volume of a gas, and the very great extent to which this may be carried out suggests that the volume occupied by the molecules is only a very small fraction indeed of the whole volume of the gas. As stated above, the molecules of a gas are in a state of rapid vibration in the process of which they are continually striking the walls of the containing vessel. The force of these impacts gives rise to the pressure exerted by the gas.

These general ideas may be expressed more precisely in mathematical form by means of the *Kinetic Theory of Gases*.

In a cubical vessel with sides l cm long let there be n molecules of gas, each of mass m, and let the pressure of the gas be p. Then if there are n molecules which at any given instant have velocities c_1, c_2, c_3, . . . c_n the so-called *root mean square velocity*, which is used instead of the average velocity of the whole group of molecules, is given by the expression—

$$c = \sqrt{\frac{1}{n}(c_1^2 + c_2^2 + c_3^2 + \ldots c_n^2)} \quad . \quad . \quad . \quad (1)$$

where c = root mean square velocity.

The root mean square velocity may be regarded as made up of three component velocities, x, y and z, parallel to the sides of the cubical vessel, *ABCDEFGH* (Fig. 23), and these are related to the root mean square velocity by the equation (1).

$$c^2 = x^2 + y^2 + z^2 \quad . \quad . \quad . \quad . \quad (2)$$

Suppose a particle starts with a velocity x from the face *ABCD*. It will ultimately strike the face *EFGH* and be reflected back again in the opposite

direction. Since the mass of the particle is m and its velocity x, its momentum just previous to striking face $ABCD$ will be mx and after striking face $EFGH$ its momentum will be $-mx$ since the particle is moving in the reverse direction; therefore the change of momentum during each impact is $2mx$. However, the force exerted upon the walls of the vessel is measured by the rate of change of momentum. Therefore, since the particle is moving with a velocity x, and no loss of time occurs during collisions, it will strike the face $EFGH$ (or the opposite face, $ABCD$) x/l times per second, so that the change of momentum giving the force exerted on the faces $ABCD$ and $EFGH$ is $2mx \times x/l = 2mx^2/l$.

Arguing in a similar manner, if the particle possessed only the component y, of its velocity, it would exert a force of $2my^2/l$ on the faces $ABFE$ and $DCGH$; and if it only possessed the component z, it would exert a force $2mz^2/l$ on the faces $AEHD$ and $BFGC$. Adding all these forces together the total force exerted by one molecule on all the six faces of the cubical vessel is $2m(x^2 + y^2 + z^2)/l = 2mc^2/l$ where c = root mean square velocity.

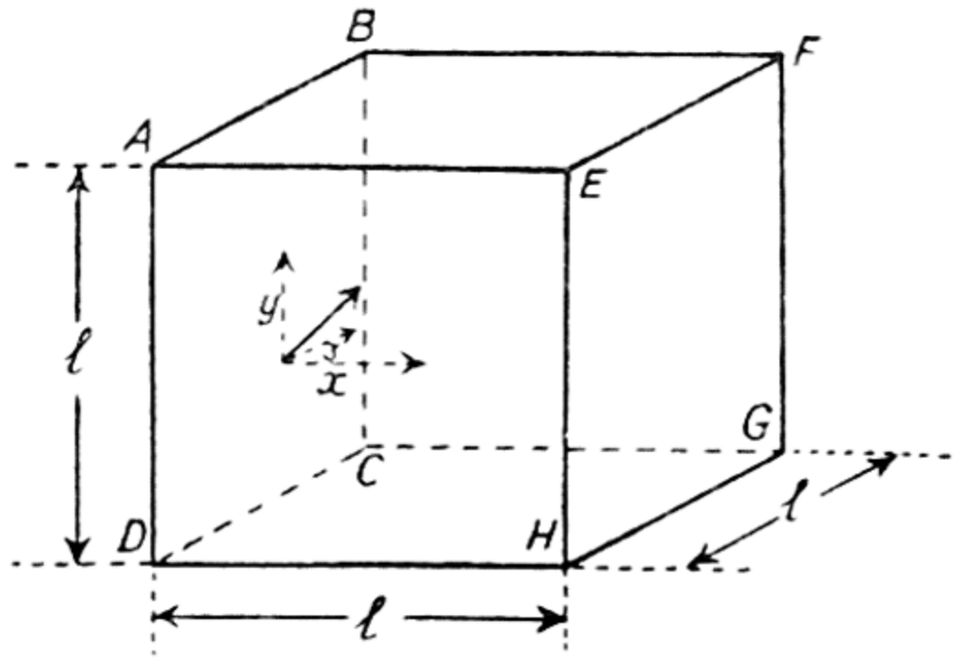


FIG. 23. Diagram illustrating Development of Fundamental Kinetic Equation

If there are n particles present, and neglecting the effect of collisions of the molecules with one another as far as effects on the walls are concerned, the total force upon the walls is $2nmc^2/l$. Therefore the pressure (or force per unit area) is evaluated by dividing this quantity by the area of the six faces, that is $6l^2$, thus—

$$\text{Pressure} = \frac{2nmc^2}{l \times 6l^2}$$

$$= \frac{2nmc^2}{6l^3}$$

and, if l^3 be the volume of a cube, V, which is the volume occupied by 1 g.mol, then n = the Avogadro number, and

$$\text{Pressure} = \tfrac{2}{6}\frac{nmc^2}{V}$$

$$\therefore \qquad PV = \tfrac{1}{3}\, nmc^2 \qquad . \quad . \quad . \quad . \quad (3)$$

and

$$PV = \tfrac{1}{3}\, Mc^2 \qquad . \quad . \quad . \quad . \quad (3a)$$

Thus, (3) is the fundamental kinetic equation. Although equation (3) has been deduced for a vessel of cubical shape it may be extended to a vessel

of any shape, since the latter may be considered as made up of a number of small cubes. The pressures on the interior cube faces neutralize one another and so do not influence the pressure on the exterior faces of the outer cubes, which when added together constitute the boundary face of the containing vessel at which the gas pressure is measured.

Deductions from the Fundamental Kinetic Equation

Boyle's Law. If a gas is maintained at constant temperature within a closed vessel, it neither gains nor loses energy, so that the mean square velocity c^2, remains constant, and obviously n and m, the number and mass of the gas molecules, must also be constant. Thus, equation (3) may be rewritten—

$$PV = \text{a constant}$$

This is the mathematical expression of Boyle's Law which has thus been deduced from the kinetic theory of gases.

Charles's Law. Equation (3) may be rewritten as follows—

$$PV = \tfrac{2}{3} \times \tfrac{1}{2}\, nmc^2$$

By definition kinetic energy is given by the expression $\frac{1}{2}mc^2$ so that for n molecules the kinetic energy is $\frac{1}{2}nmc^2$. But by the gas equation

$$PV = RT \text{ (for 1 g.mol.)} \quad . \quad . \quad . \quad . \quad (4)$$

Therefore $$\tfrac{2}{3} \times \tfrac{1}{2}\, nmc^2 = RT$$

or, $$\tfrac{2}{3} \text{ (kinetic energy of the molecules)} = RT$$

Therefore, $$\text{kinetic energy of the molecules} = \tfrac{3}{2}\, RT \quad . \quad . \quad (5)$$

or, in words, the kinetic energy of the gas molecules is proportional to the absolute temperature. This obviously is the interpretation of Charles's Law in terms of the kinetic theory. The temperature of a gas may therefore be measured by the average kinetic energy of translation of its molecules. The term "translation" is included in order to exclude other forms of kinetic energy (e.g. energy of rotation).

Avogadro's Hypothesis. If equal volumes of two gases at the same temperature and pressure are allowed to mix there is in most cases no change in temperature. Therefore, the average kinetic energy of the molecules must be the same for both gases. Thus, if these equal volumes contain in the case of one gas, n_1 molecules of mass m_1 and velocity c_1, whilst in the case of the other gas there are n_2 molecules of mass m_2 and velocity c_2, then, recalling that the kinetic energies are equal,

$$\tfrac{1}{2}m_1{c_1}^2 = \tfrac{1}{2}m_2{c_2}^2 \quad . \quad . \quad . \quad . \quad (6)$$

But since equal volumes of the two gases were taken, both at the same pressure, then—

$$p_1v_1 = p_2v_2 \quad . \quad . \quad . \quad . \quad (7)$$

and, therefore—

$$\tfrac{1}{3}n_1m_1{c_1}^2 = \tfrac{1}{3}n_2m_2{c_2}^2 \quad . \quad . \quad . \quad . \quad (8)$$

Dividing (7) by (8), it follows that

$$n_1 = n_2$$

or, expressed in words, equal volumes of different gases at the same temperature and pressure contain the same number of molecules. This, it will be recalled, is the verbal expression of Avogadro's Hypothesis (*see* p. 9).

Graham's Law of Diffusion. It has previously been established (*see* p. 85) that—

$$PV = \tfrac{1}{3}\ nmc^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\therefore \qquad c^2 = \frac{3PV}{nm}$$

but, since density, d, is equal to weight per unit volume, that is, nm/V then

$$c^2 = \frac{3P}{d}$$

i.e.

$$c = \sqrt{\frac{3P}{d}} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Therefore

$$c \propto 1/\sqrt{d} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Therefore, at constant pressure and temperature the velocity of gas molecules is inversely proportional to the square root of the density of the gas. The rate of diffusion of a gas escaping from a small orifice through a porous plug is obviously dependent upon the velocity with which the gas molecules are moving, the term c in equation (9). The kinetic theory of gases thus accounts for Graham's Law of Diffusion which states that the rate of diffusion of a gas is inversely proportional to the square root of its density.

Mean Velocity of Gas Molecules. The substitution of the appropriate values in equation (9) permits of the evaluation of the mean velocity of the molecules of a gas. Taking oxygen as example, the mean velocity of oxygen molecules is—

$$c = \sqrt{\frac{3 \times 1\,014\,000}{0{\cdot}001429}}$$

$$= 46\,100 \text{ cm/sec } (0{\cdot}3 \text{ miles/sec})$$

since P = 1 atmosphere = 76 cm of mercury

$= 76 \times 13{\cdot}6 \times 981$ dynes/cm^2

$= 1\,014\,000$ dynes/cm^2

$d = 1{\cdot}429$ g/litre $= 0{\cdot}001439$ g/cm^3

Specific Heats of Gases

It has already been shown (*see* equation (5), p. 86) that

$$\text{kinetic energy of gas molecules} = \tfrac{3}{2}RT$$

Thus, if one gramme molecule of a gas is heated within a closed vessel from T°K to $(T + 1)$°K, then the kinetic energy undergoes a corresponding increase from $\frac{3}{2}RT$ to $\frac{3}{2}R(T + 1)$, an increase of $\frac{3}{2}R$ or 3 cal., since R is equal to 2 approximately.

Now the specific heat of a gas is the number of calories which must be supplied to raise the temperature of one gramme of the gas through 1°C, and the molecular heat of a gas is the number of calories which must be supplied to raise the temperature of one gramme-molecule of the gas through 1°C.

If the only effect of application of heat is to increase the energy of translation of the molecules then the molecular heat at constant volume, C_v, should be equal to 3 cal. for all gases as derived above. It must be remembered, however, that many molecules are polyatomic and some of the energy will be associated with other forms of energy, such as that associated with the rotation of the molecule, and with the vibration of the atoms within it. The molecular heat of a polyatomic gas is therefore described by the following expression—

$$C_v = 3 + x \text{ cal.} \quad . \quad . \quad . \quad . \quad (11)$$

in which x represents the number of calories absorbed in increasing the rotational and vibrational energies of the molecules contained in one gramme-molecule of the gas. The value of x will vary from gas to gas, its value increasing with the increasing complexity of the gas molecule.

If one gramme-molecule of a gas maintained at constant pressure has its temperature raised by 1°C, then the heat imparted to the gas increases the kinetic energy of the molecules, the rotational and vibrational energies of the molecule and also provides energy equivalent to the work performed by the gas when it expands against the pressure to which it was subjected, since if the gas is heated at constant pressure instead of at constant volume then it must expand during the heating process. Thus, the molecular heat of a polyatomic gas at a constant pressure, C_p, is described by the expression—

$$C_p = 3 + x + W \quad . \quad . \quad . \quad . \quad (12)$$

in which W represents the work performed, expressed in calories, by the gas against the constant pressure when its volume is increased by an increment corresponding to a rise in temperature of 1°C.

If it be imagined that the gas is confined within a vessel closed by a movable piston held down by the pressure, P, then by application of the

gas equation, $PV = RT$, the expansion of one gramme-molecule when heated through 1°C is—

$$\frac{V}{T} = \frac{R}{P}$$

and since, W (work done) = Pressure × Increase of volume

then
$$W = P \times \frac{R}{P}$$
$$= \frac{R}{2} \text{ cal.}$$

Thus, the molecular heat at constant pressure, C_p, for one gramme-molecule of an ideal gas is given by the expression—

$$C_p = 3 + 2 \text{ cal.}$$
$$= 5 \text{ cal.}$$

In this evaluation, however, the heat used up in performing internal work upon the gas molecules has been neglected so that for the general case it is necessary to state that

$$C_p = 5 + x \text{ cal.} \quad . \quad . \quad . \quad . \quad (13)$$

in which x represents the number of calories absorbed in increasing the rotational and vibrational energies of the molecules contained in one gramme-molecule of the gas, the value of x increasing with increasing complexity of the molecule.

If S_v represents the specific heat of a gas at constant volume, S_p the specific heat at constant pressure and M the molecular weight of the gas, then

$$C_v = S_v M \text{ and } C_p = S_p M$$

therefore,
$$\frac{C_p}{C_v} = \frac{S_p M}{S_v M} = \frac{S_p}{S_v} \quad . \quad . \quad . \quad . \quad (14)$$

or, in words, the ratio of the molecular heats of a gas is equal to the ratio of the specific heats of the same gas.

Since C_v is equal to $\frac{3}{2}R$ and $C_p - C_v$ is equal to R (i.e. 2), it follows that C_p is $\frac{5}{2}R$ and the ratio of the molecular heats (or the specific heats) of an ideal gas, often represented by the symbol, γ, should be

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1{\cdot}666$$

For real gases, however

$$\gamma = \frac{C_p}{C_v} = \frac{5 + x}{3 + x}$$

so that as the value of x increases, the value of γ decreases, and, for very large values of x, γ becomes equal to nearly unity. Table 13 gives some typical values for C_p C_v and for γ.

TABLE 13

Molecular Heats of Gases

Gas	C_p (calories)	C_v (calories)	$\gamma = \frac{C_p}{C_v}$
Helium	4·97	2·98	1·69
Argon	4·97	2·98	1·67
Hydrogen	6·86	4·87	1·41
Oxygen	7·04	5·04	1·40
Nitrogen	6·93	4·93	1·41
Carbon monoxide	6·94	4·94	1·40
Chlorine	8·04	5·93	1·36
Carbon dioxide	8·79	6·75	1·30
Ammonia	8·74	6·67	1·31
Acetylene	8·88	6·83	1·28
Ethylene	10·25	8·20	1·25
Ethane	11·47	9·40	1·22

From Table 13 it will be noted that the values of γ for the inert gases helium and argon agree closely with that for an ideal gas and the heat applied in raising the temperature of these gases is therefore expended in increasing the translational velocity of the molecules, and not in increasing their internal energy. Other monatomic gases which behave in the same manner as helium and argon are the vapours of the alkali metals and of mercury. Diatomic gases have larger numerical values of C_p and C_v, but the internal work x is still equivalent to approximately 2 cal., and the value for γ therefore falls to $\frac{7}{5} = 1{\cdot}40$; whilst for triatomic molecules the value of γ is $\frac{8}{6} = 1{\cdot}33$. For yet more complex molecules the value of γ falls still further, approaching unity, so indicating that the heat absorbed within the molecule is very large compared with the work done externally by the gas undergoing expansion.

Modifications of the Kinetic Theory for Real Gases

Real gases do not behave in conformity with Boyle's Law as is emphasized by Fig. 24, in which the values of PV at one atmosphere pressure are taken as unity in each case. Experimental work has shown that Boyle's Law is not an exact law, but a limiting law which describes the behaviour of a gas more and more closely as the pressure is reduced.

From Fig. 24 it will be noted that for most gases at constant temperature, the product PV at first decreases with increasing pressure, then passes through a minimum, and finally increases as the pressure rises to higher and higher values. Certain gases, such as hydrogen, helium and neon, are less compressible at ordinary temperatures than the "ideal" gas, but, as the temperature of these gases falls, the shape of the PV-P curve changes, and in each case eventually conforms to the general case in which, as the pressure rises, the numerical value of the product, PV, at first falls, then passes through a minimum and finally increases. In the case of gases composed of complex molecules the deviations from Boyle's Law become considerable.

At low pressures all gases behave in nearly the same manner when subjected to variations of temperature and pressure and the dependence of the volume of a gas upon these two factors is expressed mathematically by the so-called "ideal" or "perfect" gas equation—

$$PV = nRT \quad . \quad . \quad . \quad . \quad (15)$$

Whereas a hypothetically "perfect" gas obeys exactly the gas equation (15), real gases do not do so for two reasons. First, the gas molecules have themselves a definite size; in other words at very small intermolecular distances two gas molecules suffer strong mutual repulsion with the result that it is not possible for more than one molecule to occupy a certain fraction of the vessel containing the gas. In order to allow for the space actually occupied by the gas molecules, van der Waals suggested that a correction term bn, known as the *co-volume* must be subtracted from the measured volume, V, in the ideal gas equation, (15). The corrected volume is thus $(V - bn)$.

The second reason for real gases not obeying the "perfect" gas equation is to be found in the small attractive forces which gas molecules have for one another. In the interior of a gas, a molecule is subjected to molecular attractions equally in all directions; consequently there is no resultant attractive force upon the molecule in question; on the other hand, in the case of a molecule at the surface of the containing vessel, the attractive force exerted by neighbouring molecules is from one side only and this force tends to pull the molecule inwards. Thus, at the instant any single molecule is on the point of striking the wall of the containing vessel and so adding its share towards the total gas pressure, the molecules in the main body of the gas exert a force having the effect of drawing that molecule away from the vessel wall. This attractive force is dependent upon the number of molecules in the body of the gas, in other words, it is proportional to the density of the gas.

In addition, the number of molecules striking the vessel wall at one instant will also be proportional to the density of the gas so that the total attractive force is proportional to the square of the density of the gas. The

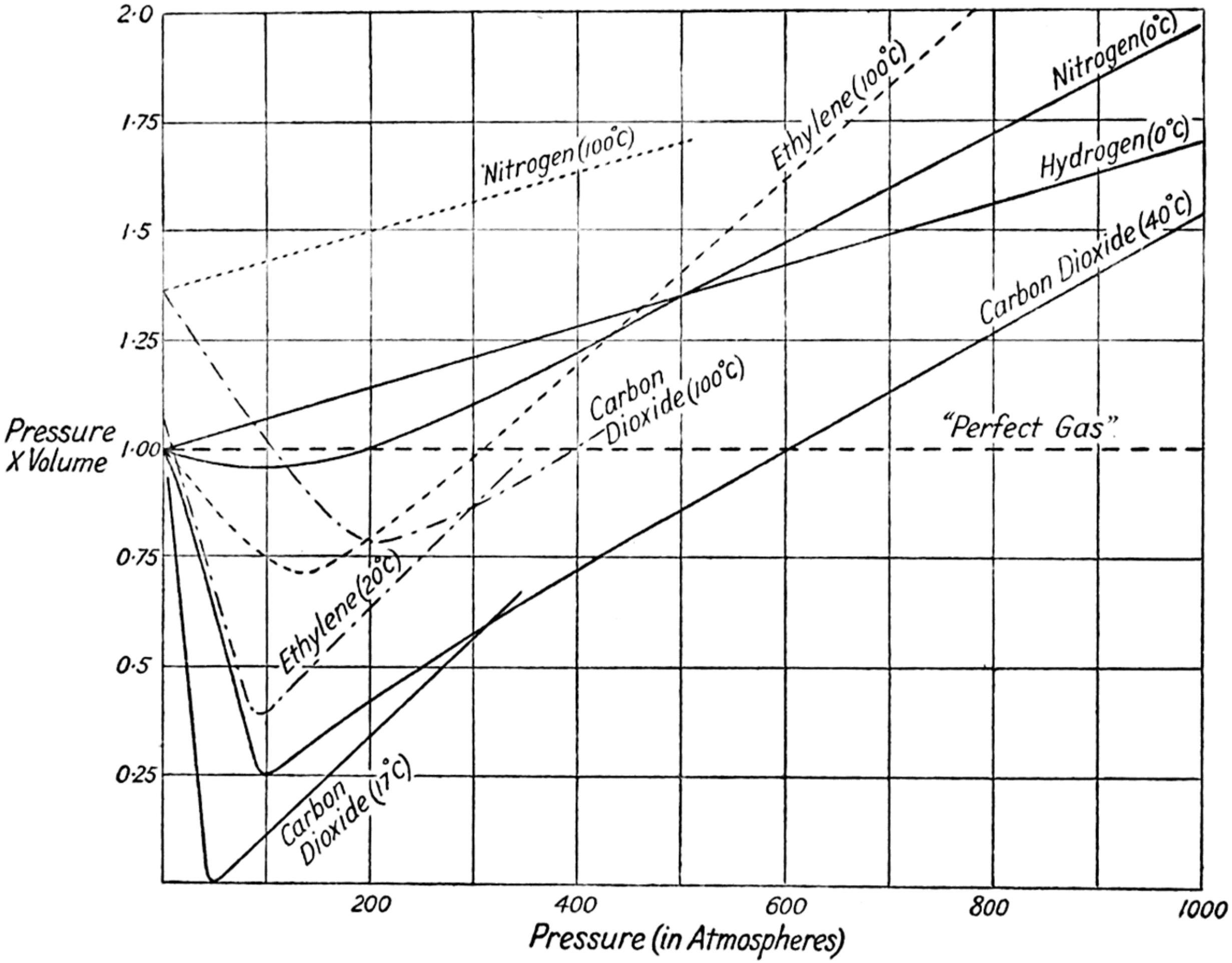


FIG. 24. Relationship of Pressure and the Product of Pressure and Volume

net result is that the measured pressure—the term P of the gas equation—is less than the ideal pressure capable of calculation from kinetic theory, and a correction term P_a, dependent upon these two factors, must be added to P. The "ideal" pressure is thus equal to $(P + P_a)$. If V is the volume occupied by one mole of a gas, then the density, d, is proportional to n/V, and it follows that—

$$P_a \propto d^2 \propto \frac{n^2}{V^2} \quad . \quad . \quad . \quad . \quad (16)$$

and,

$$P + P_a = P + \frac{an^2}{V^2} \quad . \quad . \quad . \quad . \quad (17)$$

where a = a proportionality constant.

The term an^2/V^2 is a measure of the attractive force of the molecules and is termed the *cohesion pressure*; it is of importance in connexion with the properties of liquids.

The product of the "ideal" pressure and volume of one mole of a gas should, therefore, be equal numerically to RT, in other words

$$\left(P + \frac{an^2}{V^2}\right)(V - bn) = nRT \quad . \quad . \quad . \quad (18)$$

This expression, termed *van der Waals' equation*, is one of the best-known equations of state for real gases. Some typical values for van der Waals' constants are given in Table 14.

TABLE 14

Van der Waals' Constants in Litre-atmospheres per Mole

Gas	a	b	Gas	a	b
Hydrogen . .	0·245	$2{\cdot}67 \times 10^{-2}$	Hydrogen chloride	3·8	$4{\cdot}1 \times 10^{-2}$
Helium . .	0·034	$2{\cdot}36 \times 10^{-2}$	Ammonia . .	4·0	$3{\cdot}6 \times 10^{-2}$
Nitrogen . .	1·38	$3{\cdot}94 \times 10^{-2}$	Ethylene . .	4·4	$5{\cdot}6 \times 10^{-2}$
Oxygen . .	1·32	$3{\cdot}12 \times 10^{-2}$	Chlorine . .	5·5	$4{\cdot}9 \times 10^{-2}$
Carbon dioxide .	3·66	$4{\cdot}28 \times 10^{-2}$	Sulphur dioxide .	6·7	$5{\cdot}6 \times 10^{-2}$

It will be recalled that a "perfect" gas would strictly obey Boyle's Law and this fact is indicated in Fig. 24 by the horizontal line drawn through unit value for the product, PV. All real gases, however, show departure from Boyle's Law. At very low pressures these deviations are negligible. In the case of pressures of a few atmospheres the deviations are shown to be positive for hydrogen at 0°C, and negative for nitrogen also at 0°C. Thus, if equal volumes of hydrogen and nitrogen were taken at a very low pressure, on raising the pressure of each of these gases to one atmosphere they

would be found to occupy different volumes. The hydrogen would occupy a greater volume than would a "perfect" gas at one atmosphere, whilst the nitrogen would occupy a less volume than that occupied by a "perfect" gas. Gases like hydrogen, which are less compressible than a "perfect" gas are termed "over-perfect" gases, whilst gases like nitrogen are termed "under-perfect" gases.

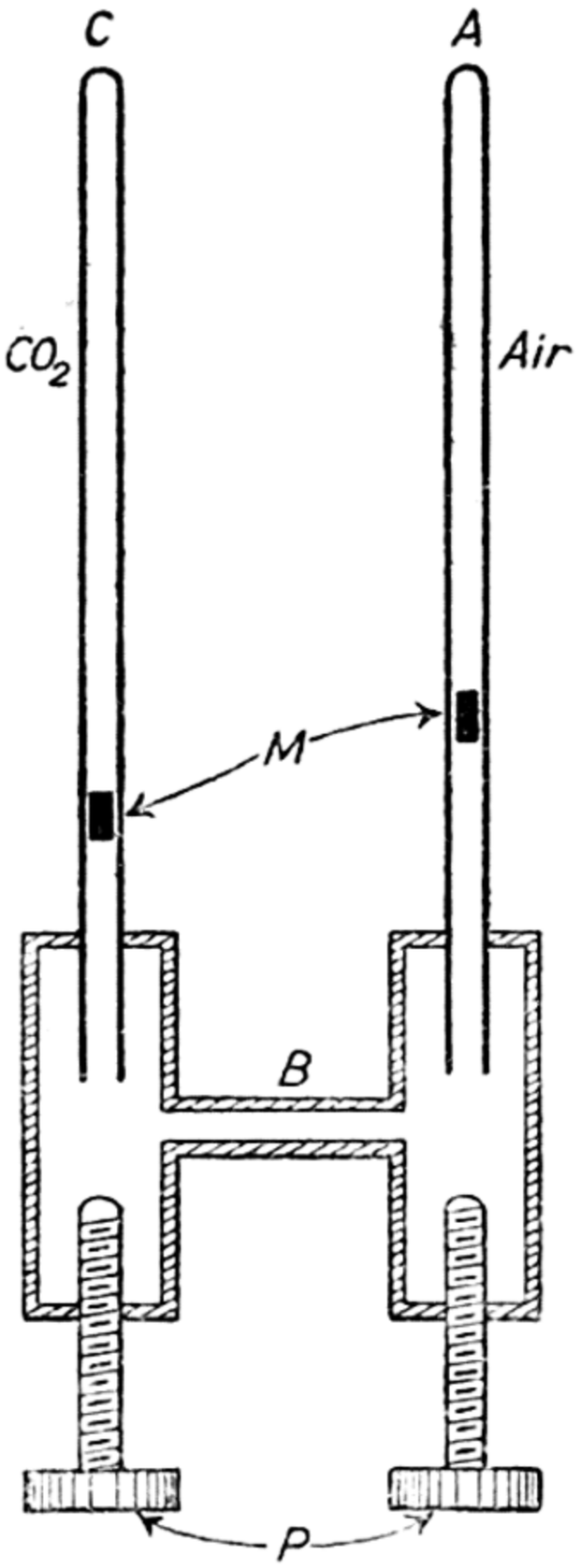


FIG. 25. Andrews' Apparatus for Determining Critical Data for Carbon Dioxide

It will thus be apparent that at atmospheric pressure Avogadro's Hypothesis is only approximately true, holding good only at those very low pressures at which, to all intents and purposes, real gases behave as "perfect" gases.

In a similar manner it can be shown that Gay-Lussac's Law of Gaseous Volumes is only approximately true at atmospheric pressure, but since deviations from this law are accounted for exactly by the deviations from Boyle's Law it may be assumed that Gay-Lussac's Law of Gaseous Volumes, like Avogadro's Hypothesis, would be strictly obeyed by real gases at very low pressures. At higher pressures (i.e. over 300 atmospheres) nitrogen at 0°C, behaves similarly to hydrogen at 0°C, in that it gives higher values for the product, PV, than that given by a "perfect" gas.

The effect of temperature variation upon the shape of the PV-P curve is to be noted here. It will be observed from Fig. 24 that the curve for nitrogen at 0°C, exhibits a clearly marked minimum whilst the curve for this gas at 100°C does not exhibit a minimum.

This effect is to be observed even more clearly in the case of carbon dioxide which shows a minimum when at 100°C, whilst when at a temperature of 17°C a sharp minimum is exhibited at 55 atmospheres at which pressure the gas liquefies. In general, the minimum on the PV-P curve becomes more clearly marked as the conditions are approached under which liquefaction occurs. Even gases like hydrogen, which at temperatures of 0°C and above show a continuous increase of the product, PV, with increasing pressure, give at very low temperatures curves similar in type to that of carbon dioxide at room temperature.

These deviations from the gas laws, therefore, seem to bear a close relationship with the phenomenon of liquefaction of a gas.

The precise conditions necessary for the liquefaction of a gas were discovered in 1869, by Andrews, who investigated the influence of pressure and temperature upon the volume of carbon dioxide. The apparatus used

by Andrews and shown diagrammatically in Fig. 25 consisted essentially of two glass tubes, one containing carbon dioxide, *C*, the other containing air, *A*, each gas being confined by a small mercury thread, *M*. Both tubes were connected to a common compression chamber, *B*, containing water to which pressure could be applied by means of the screw plungers, *P*. The upper portions of the glass tubes were maintained at the same temperature. The volume of carbon dioxide at different temperatures and

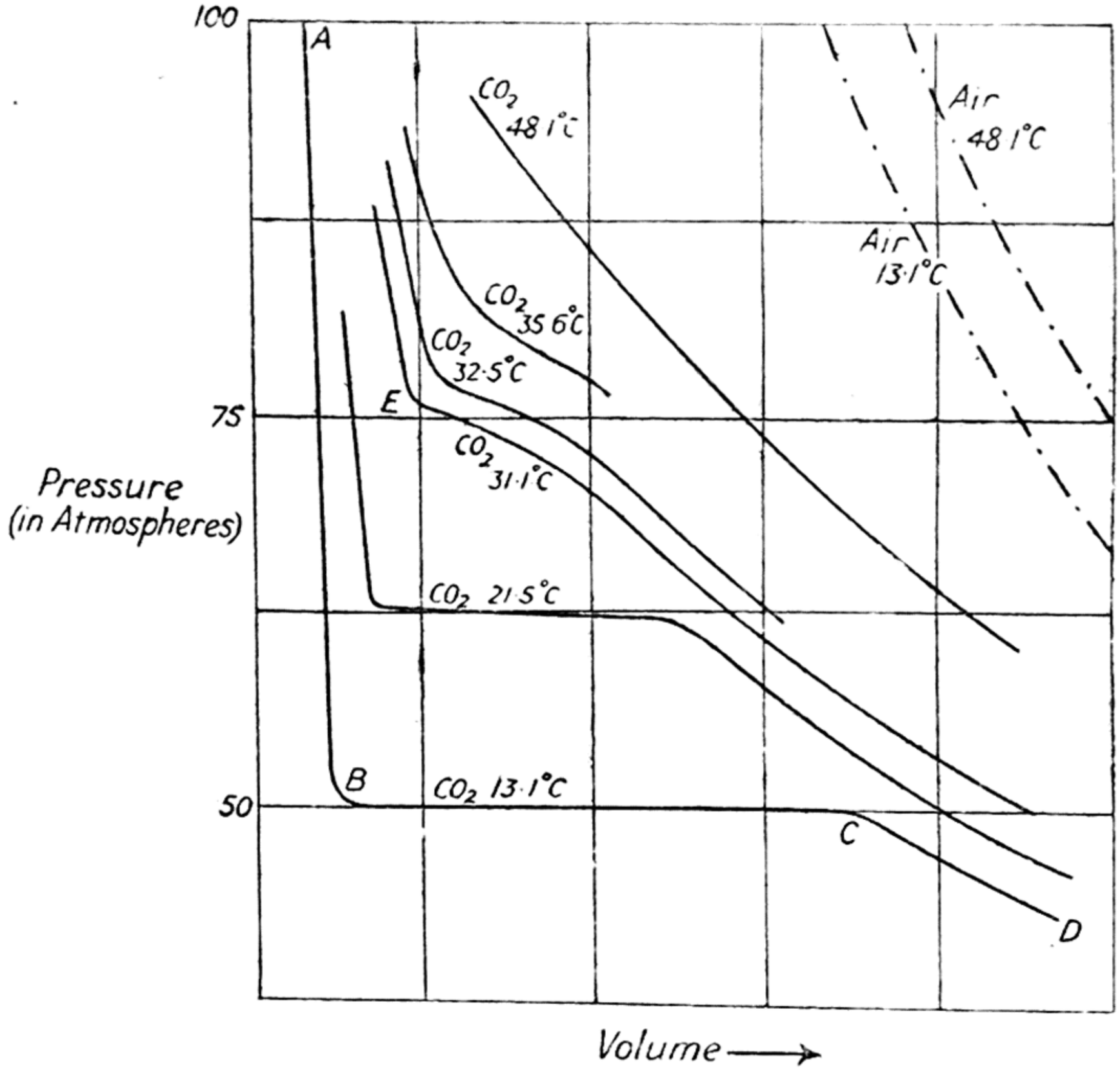


FIG. 26. Pressure-volume Curves for Air and for Carbon Dioxide

pressures was determined, the values for the pressure being calculated from the volumes of the air. The volumes of carbon dioxide—equal masses being employed in each case but at differing pressures—were then plotted in the form of isothermal curves, as shown in Fig. 26. Referring to the isothermal curve *ABCD*, at 13·1°C, it will be observed that from *D* to *C* as the pressure increases the volume decreases and the general trend of this portion of the curve *ABCD* is similar to the corresponding isothermal curve for air at 13·1°C, except that the numerical value for the product, *PV*, is less for carbon dioxide than it is for air. When the pressure attains approximately 50 atmospheres, as represented by the point *C*, liquefaction commences, as indicated by the sudden appearance of a cloud

of mist, and continues without increase of pressure* until all the gas is liquefied as indicated by the point *B*. Since liquid carbon dioxide is much less compressible than gaseous carbon dioxide, the isothermal curve then rises steeply, large pressure increases giving rise to much smaller volume increases and thus the portion *AB* is obtained.

Consideration of the next isothermal curve, that at 21·5°C, shows that a much higher pressure is necessary before liquefaction occurs and thus the horizontal portion is much shorter than is *BC* and since the gas is compressed to a much smaller volume before liquefaction commences, there is less volume change in passing from the gaseous state to the liquid state; in addition the liquid carbon dioxide at 21·5°C occupies a larger volume than liquid carbon dioxide at 13·1°C. Thus, as the temperature rises, the volume change in passing from the gaseous state to the liquid state becomes smaller and smaller, that is, the portion corresponding to *BC* becomes shorter and shorter and at a sufficiently high temperature the horizontal portion disappears altogether. This is represented by the curve for 31·1°C. At 31·1°C there is no point at which decrease in volume occurs whilst the pressure remains stationary; there is only a change in the slope of the curve. No separation of liquid carbon dioxide occurs although there is a sudden change in density in the region of the point *E*. Experimental work has shown that the highest temperature at which liquid carbon dioxide can be obtained from gaseous carbon dioxide by the application of pressure is 31·05°C. This temperature is known as the *critical temperature* for carbon dioxide. At higher temperatures, for example 32·5°C, there is still an inflexion on the isothermal curve but it becomes less and less marked as the temperature rises so that the curve for 48·1°C shows no sudden change in volume at any pressure and is similar in type to the corresponding isothermal curve for air at this temperature.

The fact that when carbon dioxide is at temperatures considerably above its critical temperature it behaves in a similar manner to air, suggests that the behaviour of air, nitrogen, hydrogen, and similar gases at atmospheric temperatures is due to the fact that they are at temperatures considerably above their critical temperatures. In actual fact, the critical temperature for nitrogen is −147·15°C, so that it is not surprising that difficulty is experienced in liquefying it. Hydrogen with a critical temperature of −239·95°C is still more difficult to liquefy; whilst helium has a critical temperature of −267·95°C, which makes it exceedingly difficult to liquefy.

The pressure required to bring about liquefaction at the critical temperature is known as the *critical pressure*; and the volume of one gramme-molecule of the substance at the critical temperature and pressure is

* In actual fact, the portion of the isothermal curve, *ABCD*, designated by *BC*, is not parallel to the volume axis, an extra pressure of about 0·25 atmosphere being necessary to complete the liquefaction.

termed the *critical volume*. At the critical point, the densities of the liquid and its saturated vapour must both be identical—this is the so-called *critical density*. The critical data for a number of common gases are given below in Table 15.

TABLE 15

Critical Data

Substance	Temperature (°K)	Pressure (Atmospheres)	Density (g/cm^3)
Helium	5·2	2·26	0·066
Hydrogen	33·2	12·8	0·031
Nitrogen	126·0	33·5	0·311
Carbon monoxide	133·6	35·5	0·311
Argon	150·7	48·0	0·510
Oxygen	154·3	49·7	0·430
Methane	190·2	45·6	0·162
Carbon dioxide	304·2	73·0	0·460
Nitrous oxide	309·6	71·9	0·454
Hydrogen chloride	324·1	81·5	0·406
Hydrogen sulphide	373·5	89·0	0·268
Ammonia	406·0	112·3	0·236
Chlorine	417·1	76·1	0·573
Sulphur dioxide	430·3	77·6	0·513

CONTINUITY OF STATE

As stated above, the densities of the liquid and saturated vapour are identical at the critical temperature; in fact, at the critical temperature the liquid and vapour become identical in all respects. This concept of the continuity of state may be approached in a different manner. If a gas at *D* (Fig. 27) is compressed isothermally at some temperature below the critical temperature, the change of volume is depicted by the curve, *ABCD*, there being a discontinuous change from gas to liquid along the line *BC* where these two phases co-exist. On the other hand, suppose the volume were maintained at the constant value as depicted by the point *D*, and the pressure increased, whilst at the same time the temperature is also increased, say, to the point *F*, and then the pressure maintained constant whilst the temperature, and consequently the volume, is decreased to *A*, then it follows that the system which was entirely gaseous at *D* is now completely liquid at *A*, both these points existing on the same isotherm. The change has been made from the gaseous state to the liquid state but there has been no sharp discontinuity indicating the sudden transition from one state to another, and at no time has there been more than one

phase present. This transition must therefore occur at the point *G*, since the critical isothermal curve is depicted by *XGY*. Thus, as the temperature is decreased from *F* to *A* the density of the gas increases so that at *G* the molecules are close enough for the forces of cohesion to cause the formation of a distinct meniscus or boundary surface. Nevertheless, the transition from the gaseous state to the liquid state is a gradual process and may therefore be regarded as a continuous transition rather than a discontinuous transition.

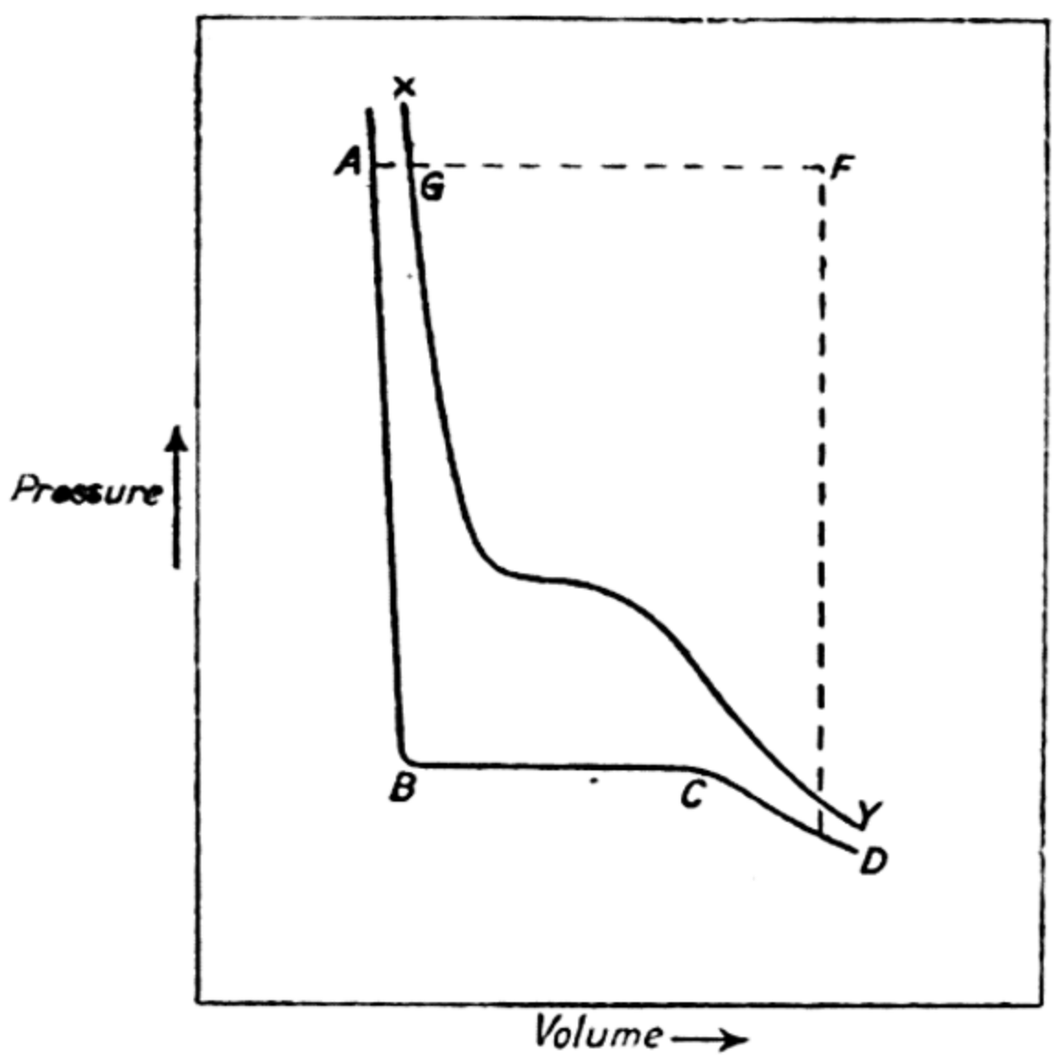


FIG. 27. Continuity of State

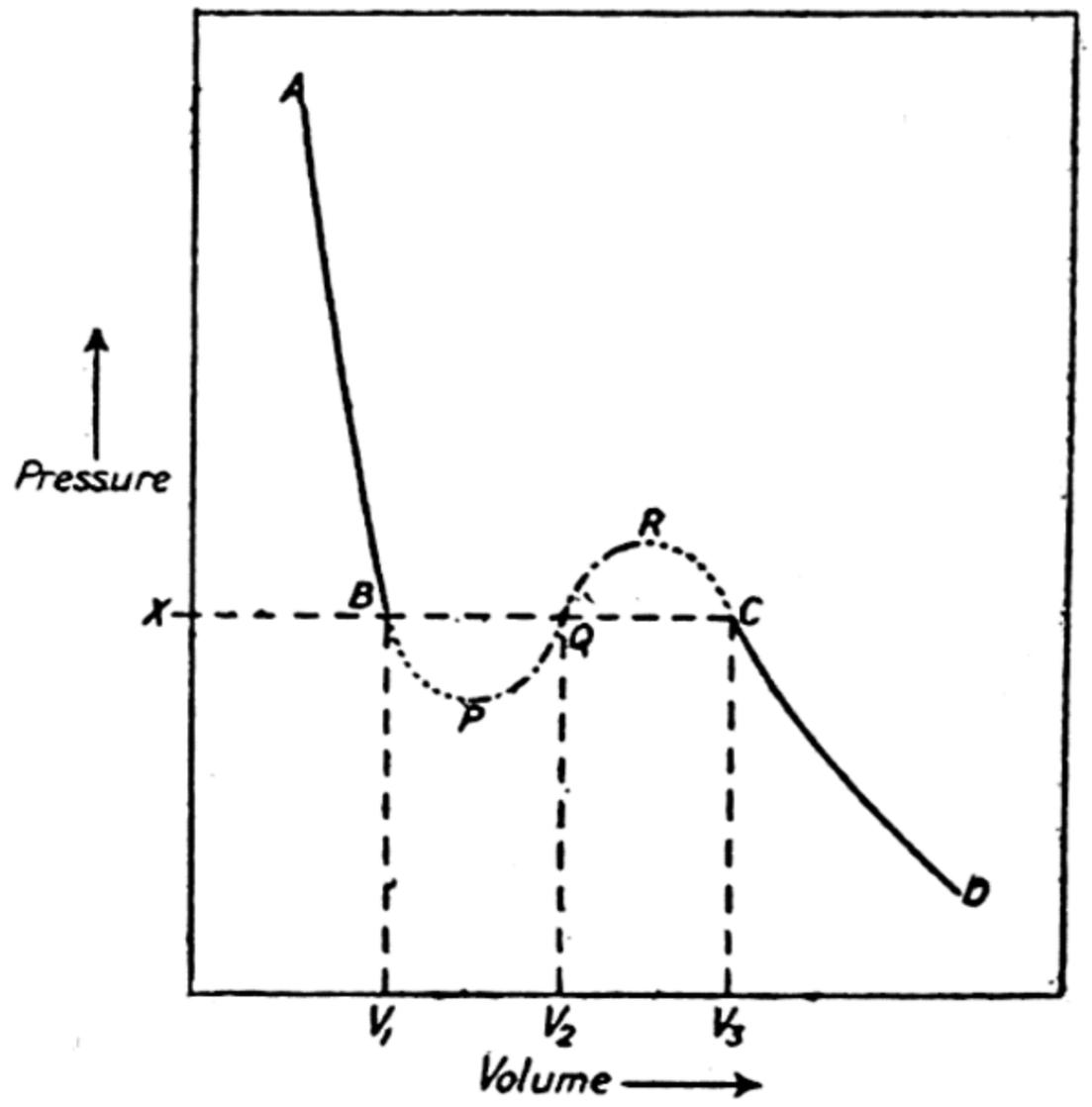


FIG. 28. Roots of Cubic Equation

Isotherms for van der Waals' Equation. If van der Waals' equation (18) be examined it will be observed that it is a cubic equation for *V*. The original form—

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

may be rewritten

$$(PV^2 + a)(V - b) = RTV^2 \quad . \quad (18a)$$

or

$$PV^3 - (bP + RT)V^2 + aV - ab = 0 \quad . \quad . \quad (18b)$$

that is

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \quad . \quad . \quad (18c)$$

A cubic equation has three roots of which either one or three are real. Thus, for any given pressure and temperature there are either one or three possible values for the volume *V*. Taking the isothermal curve for any given substance at some temperature below its critical temperature it will be true that for any pressure above the point *X* (Fig. 28) there can only be one possible value for the volume *V*; the same argument holds for any

point below the point X. On the other hand, at the point X, the volume may be V_1 (all liquid), V_2 (all vapour), or some mixture of these two states at some intermediate value. If however, a vapour is compressed in a perfectly clean and smooth vessel it is often found that the pressure at which liquefaction occurs may be exceeded without any change of the vapour into liquid. This may be represented by the line CR (Fig. 28) and any increase of the pressure beyond the point R, results in sudden liquefaction. In a similar manner if a liquid (free from dissolved air) has the pressure above it reduced, it is often possible to realize the curve, BP, although with falling pressure there will be an increasing tendency for sudden, often violent, conversion to the vapour state to occur.

The suggestion was made by James Thomson (1871) that the ideal behaviour of a gas might be depicted by the continuous isothermal curve represented in Fig. 28 by $ABPQRCD$ which thus emphasizes from another viewpoint the essential continuity of the liquid and gaseous states. The conditions between P and R cannot be realized experimentally and thus represent an unstable state. In this case the third root of the van der Waals' equation would be represented by V_3. This, however is entirely of theoretical interest and the essential point to note is that at the critical temperature the three points, B, Q and C all coincide; the values of pressure and temperature, however, must be such that the equation is in the form of a perfect cube. Thus if P_c and T_c are the critical pressure and critical temperature respectively, then—

$$V^3 - \left(b + \frac{RT_c}{P_c}\right) V^2 + \frac{a}{P_c} V - \frac{ab}{P_c} = 0 \quad . \quad . \quad (19)$$

must satisfy the condition—

$$(V - V_c)^3 = 0 \quad . \quad . \quad . \quad (20)$$

Expanding equation (20)

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \quad . \quad . \quad . \quad (21)$$

Now, equating coefficients in equations (19) and (21), the following relations may be deduced—

$$3V_c = \frac{RT_c}{P_c} + b \quad . \quad . \quad . \quad . \quad (22)$$

$$3V_c^2 = \frac{a}{P_c} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$$V_c^3 = \frac{ab}{P_c} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Thus, from equations (22), (23) and (24) the values of the critical constants may be evaluated in terms of a and b.

(1) On dividing (24) by (23),

$$V_c = 3b \quad . \quad . \quad . \quad . \quad . \quad (25)$$

or, in words, the critical volume is equal to $3b$, or van der Waals' constant b is one third of the critical volume.

(2) On substituting this value for V_c in equation (23),

$$P_c = \frac{a}{27b^2} \quad . \quad . \quad . \quad . \quad . \quad (26)$$

(3) On substituting for P_c and V_c in equation (22),

$$T_c = \frac{8a}{27Rb} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Thus, if the van der Waals' constants, a and b, are determined from measurements made on compressed gases, the values so obtained may be used to evaluate the critical constants.

THE LIQUEFACTION OF GASES

Gases may be liquefied by two methods, namely (*a*) by cooling and compression, and (*b*) by adiabatic expansion.

Liquefaction by Cooling and Compression. Those gases whose critical temperature lies below atmospheric temperature cannot be liquefied by the application of pressure alone, they are, therefore termed *permanent gases*. On the other hand, all other gases may be liquefied simply by increasing pressure but the process of liquefaction is brought about much more easily if the temperature of the gas is lowered concurrently with the increase in its pressure.

Liquefaction by Adiabatic Expansion. This method depends upon the fact that many gases are capable of cooling themselves if allowed to expand through a jet or porous plug. This is the "Joule-Thomson effect," and the numerical values for some common gases are given below in Table 16.

TABLE 16

Cooling of Some Common Gases by Expansion at 0°C

Gas	Cooling per Atmosphere of Expansion (°C)
Carbon dioxide	1·46
Oxygen	0·326
Nitrogen	0·31
Hydrogen	− 0·03

From Table 16 it will be noted that the cooling effect for the gases oxygen and nitrogen is less than for the easily liquefiable gas, carbon dioxide, these gases are, of course, under-perfect gases (*see* p. 94). On the other hand, hydrogen, an over-perfect gas, is heated slightly on undergoing expansion at 0°C.

The cooling effect for air and similar gases is small when working at 0°C, but is much more pronounced at lower temperatures, so that by arranging for a continuous circulation of the gas it is possible to attain lower and lower temperatures until, in the case of air, liquid air is finally obtained.

Compressed hydrogen, when cooled with liquid air previous to undergoing expansion, behaves like the under-perfect gases and so by utilizing liquid air as a coolant liquid, hydrogen may be prepared in a similar manner to that by which liquid air is manufactured.

By cooling helium in liquid hydrogen, and then expanding it in a similar manner to that used for the production of liquid air, it has been possible to obtain helium in the liquid state.

CHAPTER 0

THE LIQUID STATE

It has been stated previously that although a liquid has no definite shape, it has nevertheless a definite volume which is capable of being altered by the application of small forces. In terms of the kinetic theory the difference between the liquid and solid states is explained by the assumption that the molecules, which in a gas exhibit a free and independent movement with respect to one another, exist in liquids in much closer proximity with correspondingly greater intermolecular attraction.

Nevertheless, in liquids the molecules are still in a state of continuous motion and in frequent collision with one another, and therefore possess kinetic energy. Thus, if a layer of alcohol is poured carefully upon the surface of water, diffusion of these two liquids occurs and, ultimately, a single homogeneous solution is formed, so demonstrating that each of these two individual liquids possesses kinetic energy.

VAPOUR PRESSURE

It will be recalled (*see* p. 96) that if a gas is compressed isothermally at some temperature below the critical temperature, liquefaction commences when a certain pressure is attained, this pressure remaining constant as long as the gaseous and liquid phases co-exist, and rising when the gas has been liquefied completely. The pressure at which the gaseous and liquid phases may co-exist is termed the *vapour pressure* of the liquid phase at the temperature of working.

From Fig. 26 it will be noted that, as the temperature rises, so the vapour pressure suffers a corresponding rise, although an upper limit is set by the critical temperature.

If a quantity of liquid is sealed in an evacuated tube some of the liquid will evaporate until the same conditions of dynamic equilibrium obtain as would have attained had the vapour been partially condensed at the same working temperature. It is important to note that since the molecules of a liquid are in a state of continual movement, and since a liquid has an open boundary surface, some molecules will possess sufficient kinetic energy to penetrate the boundary surface and enter the space above it. This is the phenomenon of *evaporation* (*see* Fig. 29). In a closed vessel, as the number of molecules in the space above the liquid increases, there is also a tendency for molecules to return to the liquid; this is the phenomenon of *condensation*. Condensation becomes more pronounced as the number of molecules leaving the liquid increases, and thus, at any given time there will be a

condition of dynamic equilibrium when the number of molecules leaving the liquid to enter the space above it, is equal to the number of molecules returning to the liquid. The space above the liquid is then said to be saturated with vapour, the pressure exerted being the vapour pressure of the liquid at the given temperature. The magnitude of the vapour pressure of a liquid is independent of the quantity of liquid present initially, and of the volume occupied by the vapour, being only dependent upon the temperature of the liquid.

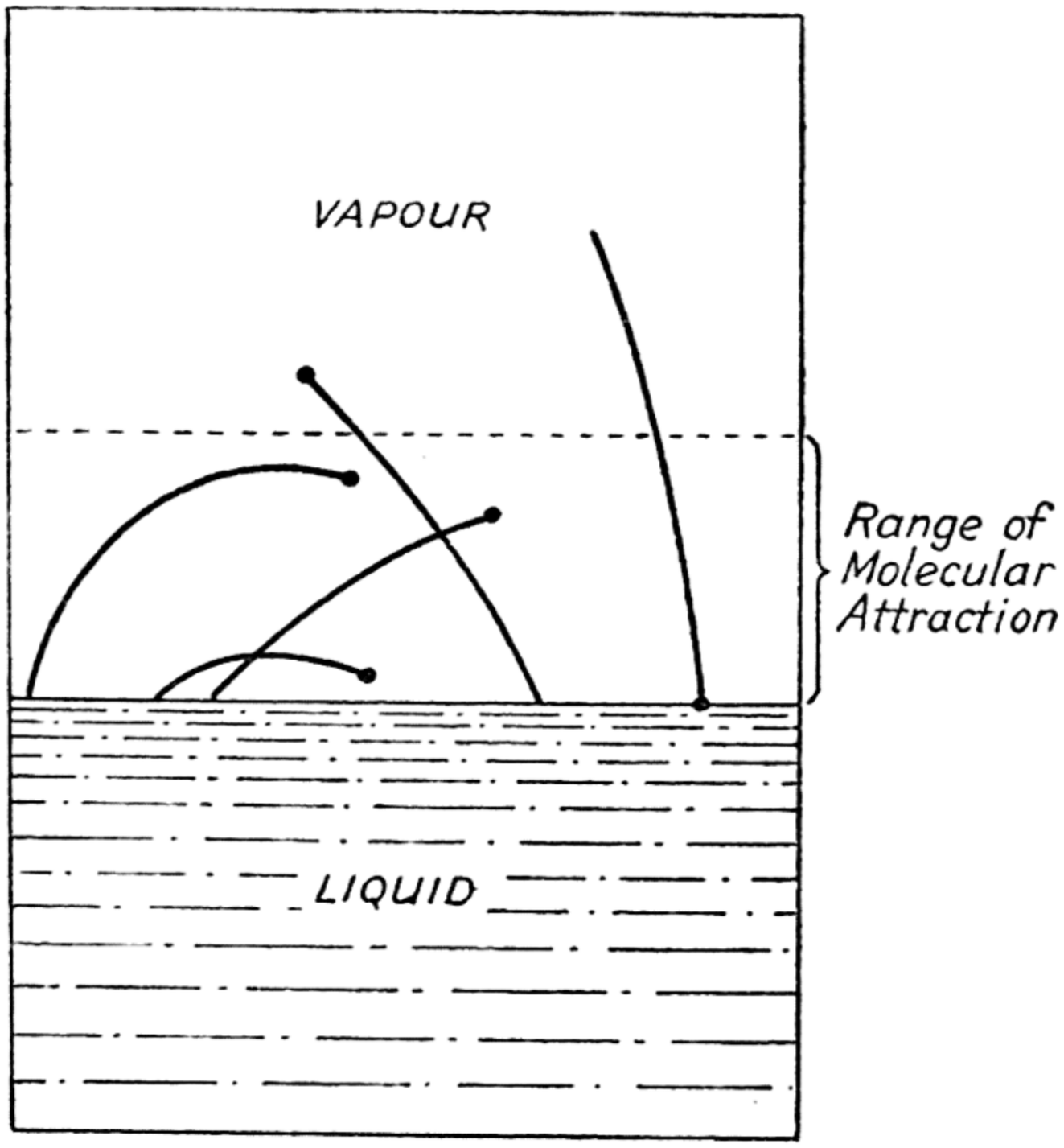


FIG. 29. Processes of Evaporation and Condensation within a Closed Vessel

Every liquid has the tendency to evaporate until the pressure of the vapour above it is the same as the equilibrium value for a given temperature, that is, the vapour pressure of the liquid. When evaporation of a liquid takes place within a closed vessel the equilibrium pressure is soon attained, but if the liquid is exposed to the atmosphere evaporation will continue until finally the whole of the liquid has passed into the gaseous state.

Latent Heat of Vaporization. On the average, molecules of vapour possess more potential than do molecules of the liquid with which the vapour is in equilibrium. In other words, the process of evaporation is accompanied in general by an absorption and condensation by an evolution of heat. Thus, when a definite quantity (say 1 g or one mole) of liquid is vaporized, the heat absorbed is termed the *latent heat of vaporization* per gramme or mole, according to the quantity of liquid taken.

Measurement of Vapour Pressure

Static Method (Ramsay and Young). The apparatus employed in this modification of the static method for determining the vapour pressure of a liquid is shown diagrammatically in Fig. 30. Fitting into the mouth of the tube *A*, is a stopper carrying a thermometer, a tap funnel and a leading tube, *F*. The thermometer bulb is covered with cotton-wool lightly tied in place with thread and the lower end of the tap funnel is bent so as to touch

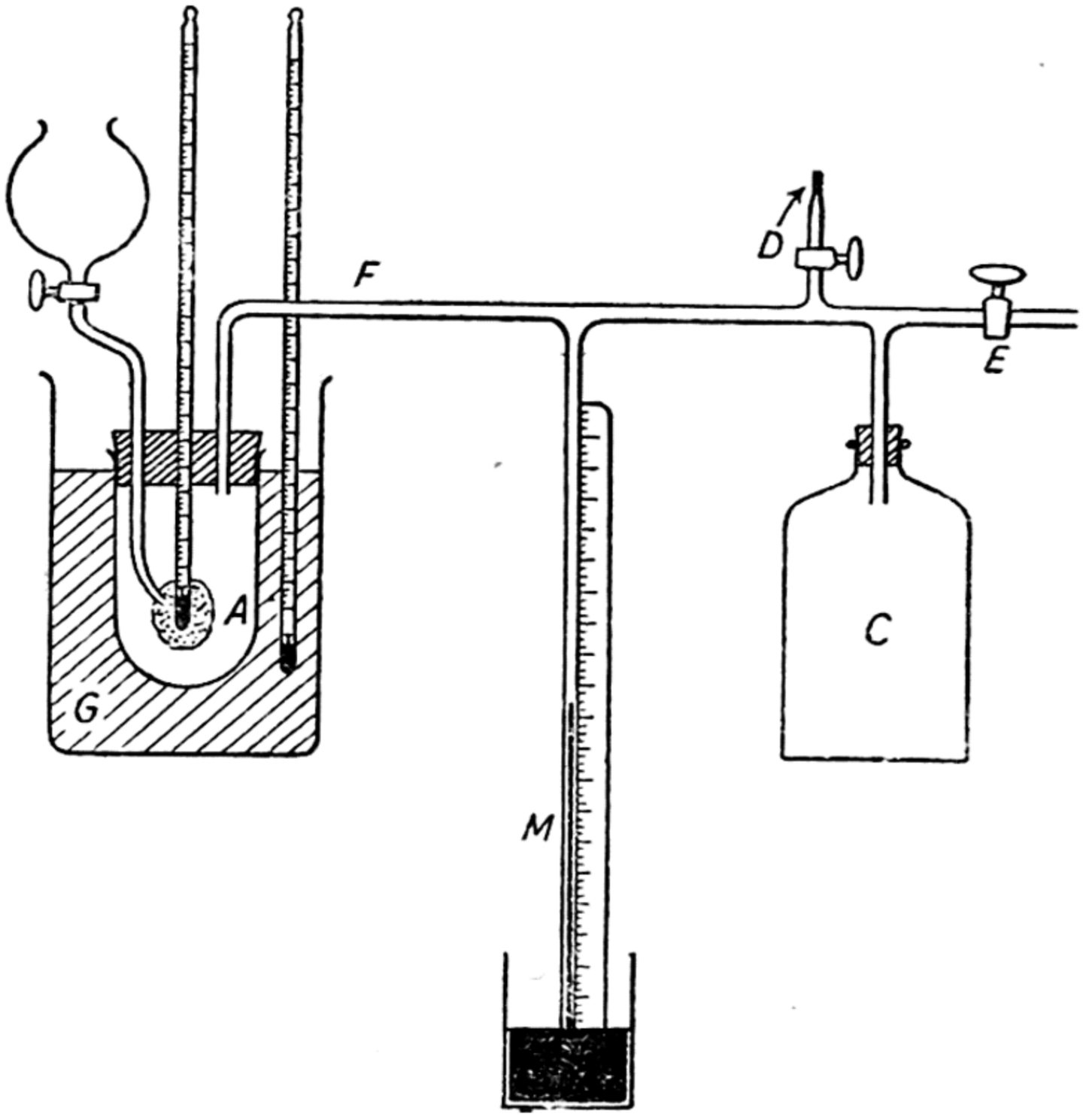


FIG. 30. Static Method for Measurement of Vapour Pressure (Ramsay and Young)

the cotton-wool. The manometer, *M*, contains mercury as the indicating medium. With the object of increasing the volume of the apparatus, and so minimizing the effect of slight leaks, a large bottle, *C*, is connected to the system. A long fine capillary, *D*, is connected to the system through a tap, the object of which is to permit the admission of air at a very slow rate when desired.

The apparatus is evacuated to about 30 mm pressure and a little of the liquid under investigation admitted to tube *A* through the tap funnel. The water bath is heated to a temperature slightly in excess of the temperature at which the vapour pressure is required to be determined. If the thermometer initially reads a higher temperature than the steady, final temperature, some of the liquid will evaporate and cool the thermometer bulb, whilst if the thermometer bulb temperature is lower than the final temperature, then

liquid will condense upon it and warm the bulb. When a steady temperature is finally attained in the bulb, *A*, this should be noted and at the same time the pressure as indicated by the pressure gauge, *M*; this latter reading, when subtracted from the corresponding barometric pressure at the time of the experiment, gives the vapour pressure at the temperature indicated by the thermometer in bulb *A*. If values of the vapour pressure at higher temperatures are then required, a little air should be admitted cautiously through the capillary *D*, the temperature of the water bath raised by the appropriate amount, and the procedure repeated as described above.

Dynamic Method (Smith and Menzies). In this method the bulb *A* of Fig. 30 is fitted with a stopper carrying a thermometer, *T*, and a leading tube, *L*, as shown in Fig. 31. A small bulb, *B*, is secured to the thermometer. The tube, *A*, is filled with a suitable liquid of high boiling-point such as medicinal paraffin. The liquid under investigation is contained within the small bulb, *B*. The rest of the apparatus is the same as that described above in Ramsay and Young's method.

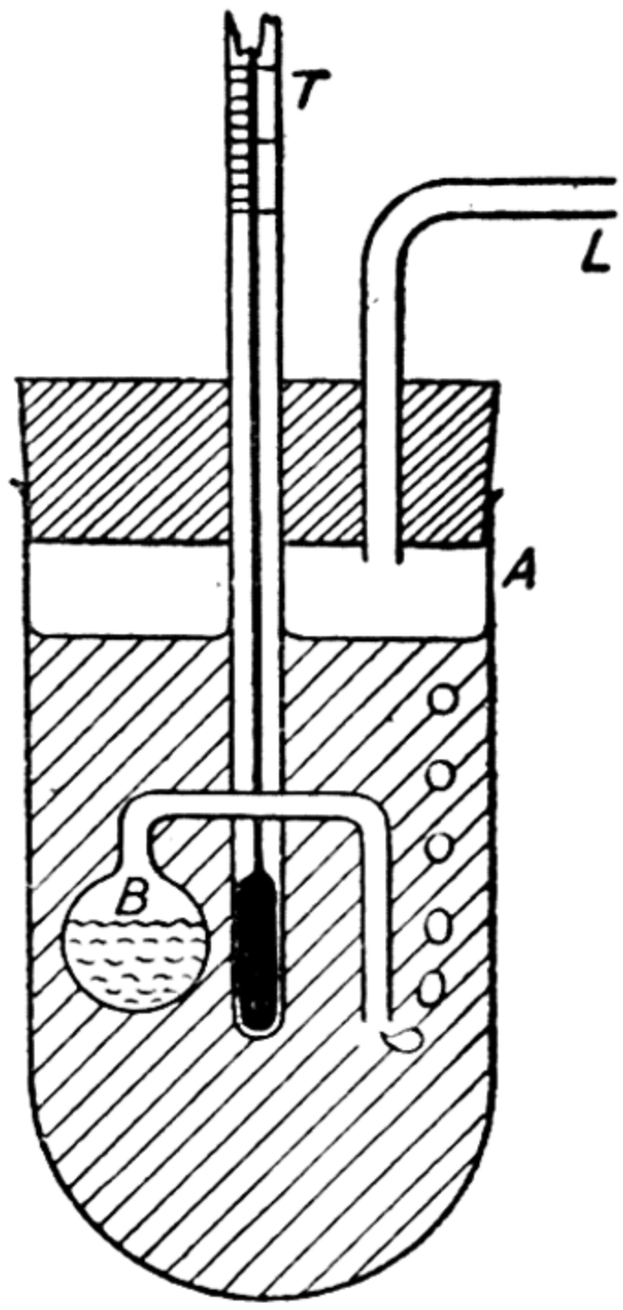


FIG. 31. Dynamic Method for Measurement of Vapour Pressure (Smith and Menzies)

In operation the temperature of the outer bath is raised to a temperature slightly in excess of that at which the vapour pressure is to be measured, and the apparatus is evacuated. It will then be noted that small bubbles issue from the bulb, *B*, as the liquid contained within boils. Whilst tap, *E*, Fig. 30, is kept closed, the fine capillary is opened and air cautiously admitted to the apparatus until bubbles of vapour just cease to issue from the bulb, *B*; then pressure gauge, *M*, and thermometer, *T*, are read. The difference between the reading of the pressure gauge and the barometric pressure gives the vapour pressure at the temperature indicated by thermometer, *T*; this vapour pressure however, must be increased by adding a correction for the depth of immersion of the bulb *B* in the liquid contained within tube *A*.

Transpiration Method. In this method dry air, or a dry gas, is slowly bubbled at constant temperature through the liquid under investigation contained within a suitable vessel. In this way the gas becomes saturated with the vapour of the liquid and the partial pressure of the liquid in the resulting gaseous mixture is equal to the vapour pressure. Assuming that Dalton's Law of Partial Pressures holds for the experimental conditions which exist, and that the vapour behaves ideally, then—

$$PV = \frac{w}{M} RT \quad . \quad . \quad . \quad . \quad (1)$$

where P = partial pressure of the vapour, V = total volume of gas, w = weight of liquid vaporized, and M = molecular weight of vapour formed in the saturated vapour.

Vapour Pressure and Temperature

The influence of temperature variation upon vapour pressure is represented by a logarithmic curve of the type shown in Fig. 32, the critical point being the highest temperature at which the vapour pressure can be measured. It will be noted from Fig. 32 that the increase per degree increases as the temperature rises. The *rate* at which the vapour pressure of a liquid varies

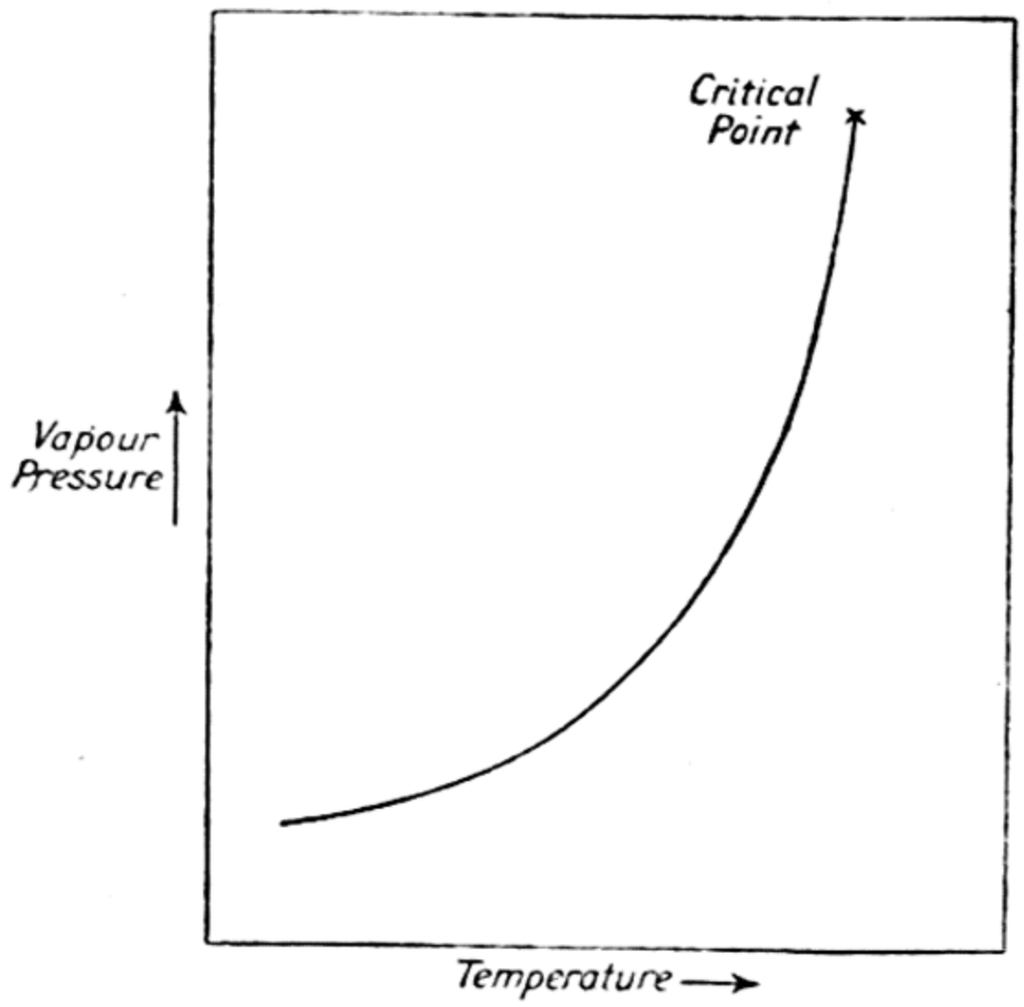


FIG. 32. Influence of Temperature Variation upon Vapour Pressure

with variation of the absolute temperature is given by the Clausius-Clapeyron equation which is derived from fundamental equations of the Second Law of Thermodynamics. In mathematical form it may be stated as follows—

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad . \quad . \quad . \quad . \quad (2)$$

where dP/dT = the rate at which vapour pressure increases with the temperature, ΔH = molar heat of evaporation, and ΔV = increase in volume accompanying the vaporization of 1 mole of liquid.

The variation of vapour pressure with temperature for a number of substances is given in Table 17.

Trouton's Rule. An important generalization known as Trouton's Rule is expressed by the formula—

$$\frac{L_e}{T_b} = \text{a constant} \quad . \quad . \quad . \quad . \quad (3)$$

where L_e = molar latent heat of vaporization of a liquid (i.e. molecular

TABLE 17

Vapour Pressure of Liquids

(*in mm mercury, unless stated otherwise*)

Temperature (°C)	Water	Ethyl Alcohol	Carbon Tetrachloride	Di-ethyl Ether	Sulphur Dioxide
10		23·6		291·7	2·256a
20		43·9	91·0	442·2	3·288a
30		78·8	141·5	647·3	4·498a
40		135·3	213·3	1·212a	6·125a
50		222·2	312·0	1·680a	8·176a
60		352·7	444·3	2·275a	10·73a
70		542·5	617·43	3·021a	13·87a
80		812·6	1·10a	3·939a	17·68a
90		1·562a	1·46a	5·054a	22·27a
100	1·000a	2·228a	1·92a	6·394a	27·71a
110	1·414a	3·107a	2·47a	7·987a	34·09a
120	1·959a	4·243a	3·20a	9·861a	41·43a
130	2·666a	5·685a	3·95a	12·05a	49·70a

Note: a = atmospheres

TABLE 18

Trouton's Rule

Substance	L_e (cal)	T_b (°K)	L_e/T_b
Helium . . .	22	4·2	5·2
Hydrogen . . .	216	20·3	10·6
Carbon monoxide . .	1 414	81·6	17·3
Nitrogen . . .	1 362	77·3	17·6
Oxygen . . .	1 610	90·2	17·9
Methane . . .	1 951	108·0	18·0
Sodium . . .	23 300	1 155·0	20·2
Carbon disulphide .	6 490	319·0	20·4
Di-ethyl ether . .	6 466	307·0	21·1
Benzene . . .	7 497	353·0	21·2
Mercury . . .	14 200	630·0	22·6
Zinc	27 730	1 180·0	23·5
Water	9 700	373·0	26·0
Ethyl alcohol . .	9 448	351·0	26·9

weight × latent heat of evaporation), T_b = boiling point of the liquid on the Absolute scale.

Some typical values for the constant as given in (3) are quoted in Table 18.

It is important to appreciate that Trouton's Rule is only empirical and approximate. It will be noted that for many non-associated* liquids the numerical value for the constant in (3) is equal to approximately 20. The generalization breaks down, however, for associated liquids (e.g. water and ethyl alcohol), for substances of high boiling point (e.g. zinc), and for substances of low boiling point and low molecular weight (e.g. helium and hydrogen).

SURFACE TENSION

Within the interior of a liquid a molecule is surrounded uniformly by other molecules with the result that it is attracted on the average with equal force in all directions. In the surface layer, however, the attraction is all from within the interior of the liquid, with the consequence that a liquid always tends to contract to the smallest possible surface area. It is for this reason that drops of liquids and bubbles of gas within a liquid tend to assume a spherical form so that the surface area is at a minimum for a given volume.

Because of this tendency to contract, a liquid surface behaves as though it were in a state of tension, being said to exhibit *surface tension*. The surface tension of a liquid is the same in all directions along the surface of the liquid. Surface tension, usually designated by the symbol, γ, is defined as the tension, in dynes, acting at right angles to any line of 1 cm length on the surface of the liquid.

Surface tension, in conjunction with the ability of a liquid to "wet" glass, causes the rise or fall of liquids in capillary tubes. Water and most organic liquids which wet glass exhibit a capillary rise since thereby the area of the wet surface is diminished. On the other hand, mercury, which does not wet glass, exhibits capillary fall resulting from which the surface area is diminished. The surface tension of liquids which wet glass may be determined from their capillary rise in a narrow tube, as follows—

Let the perimeter of the tube $= 2\pi r$

the tension supporting the column of the liquid $= 2\pi r\gamma$

the weight of column of liquid supported by this tension $= \pi r^2 hd$

where h = height of column, d = density of liquid, and r = radius of tube.

* Non-associated liquids are those which contain single molecules; conversely, associated liquids are those in which the molecules are combined together in groups of two or more, the molecular weight being thus a multiple of the simple formula weight.

Associated liquids usually have very high latent heats of evaporation, abnormally high boiling points and high dielectric constants. Associated liquids also exhibit the ability to dissociate certain solutes into ions; this is probably related to their high dielectric constants.

Then for equilibrium, $2\pi r\gamma = \pi r^2 hd$ and, expressing this in dynes

$$2\pi r\gamma = \pi r^2 hgd$$

$$\gamma = \tfrac{1}{2} rhgd \quad . \quad . \quad . \quad . \quad (4)$$

where $g = 981$ cm/sec^2.

Influence of Temperature on Surface Tension. As the temperature of a liquid rises its surface tension, in general, decreases, finally becoming zero at the critical temperature. Ramsay and Shields showed that a straight line is obtained if temperature is plotted against the quantity $\gamma \left[\frac{M}{D}\right]^{\frac{2}{3}}$ where M = molecular weight, D = density of liquid, whereas the plot of surface tension against temperature shows a pronounced curvature. The quantity $\left[\frac{M}{D}\right]$ is known as the molecular volume, and $\left[\frac{M}{D}\right]^{\frac{2}{3}}$ is a measure of the surface area of the molecules. The quantity $\gamma \left[\frac{M}{D}\right]^{\frac{2}{3}}$ is known as the molecular surface energy, and Ramsay and Shields have expressed the variation of molecular surface energy with temperature in the following equation—

$$\gamma \left[\frac{M}{D}\right]^{\frac{2}{3}} = k(T_c - t - 6) \quad . \quad . \quad . \quad . \quad (5)$$

where k = a constant giving the slope of the curve, T_c = the critical temperature, t = the temperature at which observations were made.

A much more precise relation between surface tension and temperature was proposed by Macleod as follows—

$$\gamma = C(D - d)^4 \quad . \quad . \quad . \quad . \quad (5a)$$

where D = density of the liquid under examination, d = density of the saturated vapour of the liquid measured at the same temperature, C = a constant.

VISCOSITY

It is well known that the volume of liquid capable of flowing through a given tube in unit time under constant pressure varies with the liquid, and for any given liquid it also varies with the temperature and with the type of flow, that is whether turbulent flow or "streamline" flow. Streamline flow is that in which all liquid layers move parallel to the sides of the tube.

In streamline flow the property of a liquid which determines its rate of flow is known as *viscosity*. Viscosity, therefore, is that property which opposes the relative movement of adjacent portions of a liquid, and thus may be regarded as a type of internal friction. Gases, like liquids, exhibit viscosity. The reciprocal of viscosity is termed the *fluidity* of a liquid or

gas as the case may be. The coefficient of viscosity is denoted by the symbol η, whilst fluidity is usually denoted by the symbol ϕ, thus, $\phi = 1/\eta$. The coefficient of viscosity, η, is defined as the number of dynes per square centimetre required to maintain a velocity of 1 cm/sec between layers of 1 cm^2 area and 1 cm apart. Coefficients of viscosity are generally expressed in c.g.s. units as stated above and the unit is termed a *poise* in honour of Poiseuille whose fundamental researches on viscosity have attained a classical reputation. Since the poise is often a large unit to employ, other fractional units have also been introduced, namely, the *millipoise* (i.e. 10^{-3} poise), and the *centipoise* (i.e. 10^{-2} poise).

The viscosities of liquids differ enormously, in fact certain liquids which exhibit an extremely high viscosity behave in many respects like solids. Some typical viscosities are given in Table 19.

TABLE 19

Typical Viscosities at 20°C

Substance	Viscosity (in millipoises)
Diethyl ether	2·33
Acetone	3·29
Carbon disulphide	3·68
Choloroform	5·63
Methyl alcohol	5·93
Benzene	6·47
Carbon tetrachloride	9·68
Water	10·08
Ethyl alcohol	12·00
Acetic acid	12·20
Nitrobenzene	20·13
Glycerine	approximately 1×10^4

The Determination of Viscosity

The viscosity of a liquid may be determined (*a*) by measuring the volume of the liquid flowing through a tube of given dimensions under a definite pressure, (*b*) from the rate at which a dense sphere falls through the liquid, (*c*) from the speed of rotation of a cylinder immersed in the liquid and driven by the fall of a standard weight, or (*d*) from the torsion in a standard wire supporting a cylinder immersed in the liquid revolving at a known speed. Only the first two of these methods will be described here.

Viscometer Method. This method depends upon Poiseuille's Law which states that *the rate of flow of liquid through a narrow tube is inversely*

proportional to the fourth power of the radius of the tube. In mathematical form this law is expressed as follows—

$$\eta = \frac{\pi r^4 pt}{8vl} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where η = coefficient of viscosity
r = radius of the tube
l = length of the tube
p = pressure in dynes/cm^2
v = volume of liquid in ml flowing through the tube
t = time (in sec) required for flow to occur.

This method involves the use of an instrument known as a "viscometer" or "viscosimeter" of which the type due to Ostwald is widely employed (*see* Fig. 33). The Ostwald viscometer consists essentially of a bulb, *A*, with a mark (x) above and (y) below, and attached to a capillary tube, *B*, and a storage reservoir, *C*. In use the viscometer, charged with the liquid under examination, is clamped in a vertical position in a thermostat, with the liquid levels adjusted to coincide with the marks (p) and (q). When the liquid in the viscometer has attained the temperature of the thermostat it is sucked up the left-hand limb of the viscometer until it has reached the level of the mark (x). The time required for the liquid to fall from the mark (x) to the mark (y) is then determined by means of a stopwatch. The determination is then repeated with water as a reference liquid. The relative viscosity may then be evaluated from the following expression—

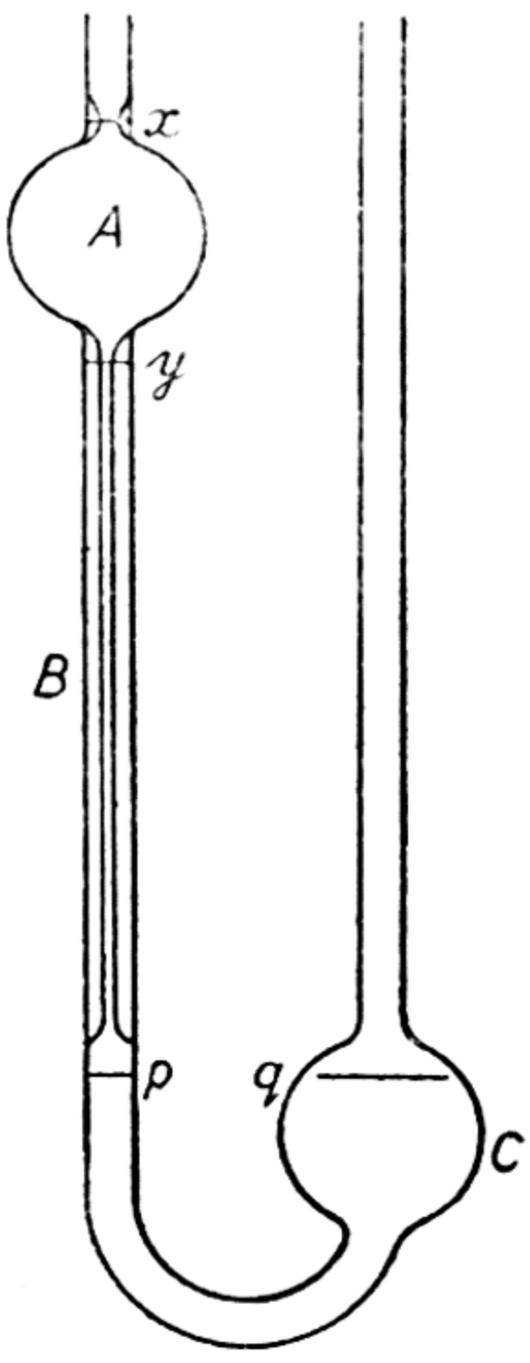


FIG. 33. Ostwald Viscometer

$$\text{Relative viscosity} = \frac{\eta}{\eta_w} = \frac{dt}{d_w t_w} \quad . \quad . \quad . \quad (7)$$

where t = time (in sec) required for liquid to flow between two marks
t_w = time (in sec) required for water to flow between two marks
η = coefficient of viscosity of liquid under examination
η_w = coefficient of viscosity of water
d = density of liquid under examination
d_w = density of water.

Although water is the most frequently used standard of reference, sometimes other liquids are employed, for example benzene. The variation of the viscosities of these two liquids with temperature is shown in Table 20.

TABLE 20

Variation of Viscosity of Water and of Benzene with Temperature

Temperature (°C)	Viscosity (in poises)	
	Water	Benzene
0	0·01793	0·009060
20	0·01008	0·006537
40	0·00657	0·004981
60	0·00469	0·003980
80	0·00356	0·003358
100	0·00284	

Falling Sphere Method. The rate of fall of a sphere through a fluid rapidly attains a constant value when the viscous force is exactly equal to the gravitational pull. By the application of Stoke's Law the relation of velocity and viscosity is given by the following expression—

$$u = \frac{2gr^2(D-d)}{9\eta} \quad . \quad . \quad . \quad . \quad (8)$$

where u = velocity of falling sphere in cm/sec
g = 981 cm/sec²
r = radius of falling sphere
D = density of sphere
d = density of liquid through which sphere falls
η = coefficient of viscosity of liquid.

Equation (8) is only strictly true when a sphere falls through a large mass of liquid. In practice this method consists of introducing a small metal sphere (e.g. a ball bearing) below the surface of the liquid under examination contained within a tall cylinder, and noting the time taken for it to fall between two marks on the cylinder.

As a means of industrial control, this method may be modified slightly and two observations taken, one with the liquid under examination and the other with a standard liquid. The relative viscosity is then evaluated by means of the following expression—

$$\text{Relative viscosity} = \frac{\eta_1}{\eta_2} = \frac{t_1(D-d_1)}{t_2(D-d_2)} \quad . \quad . \quad (9)$$

where η_1 = coefficient of viscocity of liquid 1
η_2 = coefficient of viscosity of liquid 2
t_1 = time required for sphere to fall through liquid 1
t_2 = time required for sphere to fall through liquid 2
d_1 = density of liquid 1
d_2 = density of liquid 2
D = density of falling sphere

The viscosity of all liquids decreases with falling temperature. Increasing pressure causes an increase in viscosity, especially at low temperatures.

OPTICAL PROPERTIES

Refractive Index. The refractive index of a material may be defined as the bending power of that material for a ray of light incident on its surface; this is illustrated diagrammatically in Fig. 34.

The amount of this bending, expressed as refractive index, is a characteristic property of materials and indeed may be employed for purposes of identification. The refractive index of a substance is defined as *the ratio of the sine of the angle of incidence to the sine of the angle of refraction;* this is the verbal expression of Snell's Law which, expressed in mathematical form, is—

$$\frac{\sin i}{\sin r} = n \quad . \quad . \quad (10)$$

where n = refractive index, i = angle of incidence, r = angle of refraction.

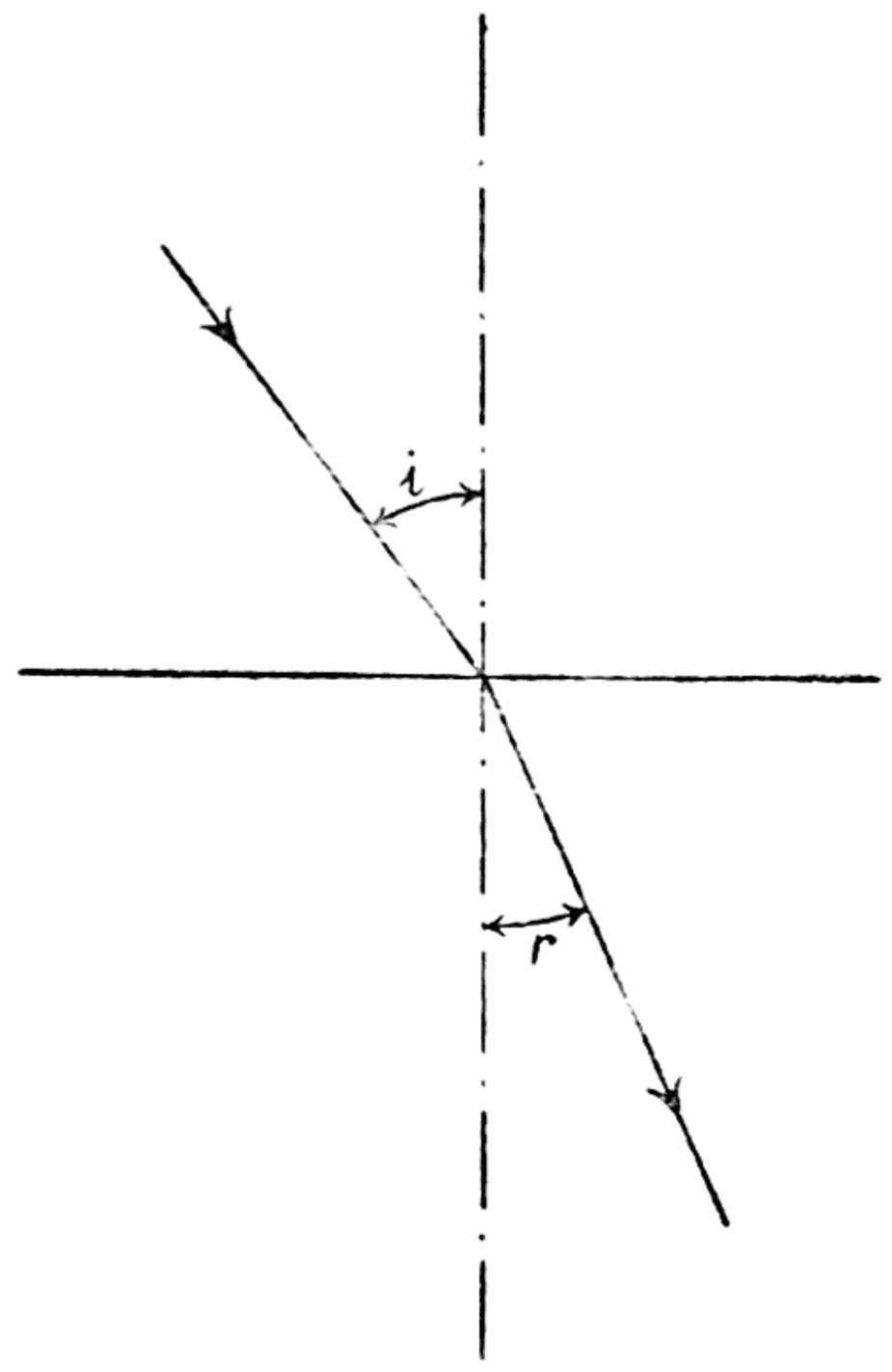


FIG. 34. The Refraction of Light

For a given material the refractive index varies with the wavelength of the light, undergoing an increase in value as the wavelength suffers a decrease. Thus, for purpose of standardization and accurate determination it is usual to employ the D line of the sodium spectrum as the basis for comparison. The refractive index of a material also varies with the temperature of the material. Lorentz and Lorenz (1880) have deduced that the following relationship should not vary with temperature—

$$\frac{(n^2 - 1)M}{(n^2 + 2)D} = [R] \quad . \quad . \quad . \quad . \quad (11)$$

where the quantity $[R]$ is the *molecular refraction.*

Various types of instruments are available for the determination of

refractive index and reference should be made to a textbook of practical optics for details regarding their use.

Absorption Spectra. Many substances, when introduced into an electric arc or a high tension spark, enter into an excited state leading to the production of line spectra capable of observation by means of a spectroscope or of photographic recording by means of a spectrograph; when light of known wavelengths, however, previous to entering a spectrograph, is allowed to traverse a column of a liquid, preferential absorption will occur at certain wavelengths. Thus are produced the so-called *absorption bands*. Such absorption bands occur in the visible, in the ultra-violet and in the infra-red portions of the spectrum.

Optical Rotation. Those substances which are capable of rotating the plane of polarization of light are said to be *optically active*, and to have *optical rotatary power*.

The *specific rotatary power* (or *specific rotation* $[\alpha]$) is expressed by the equation—

$$\frac{a}{ld} = [\alpha] \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where a = measured angle of rotation, l = length of the liquid column in decimetres, d = density of the liquid.

The specific rotation for a solution is given by—

$$\frac{100a}{ldW} = \frac{100a}{1c} = [\alpha] \quad . \quad . \quad . \quad . \quad (13)$$

where W is the weight of the substance in 100 g, and c the weight in 100 ml of solution.

The *molecular rotatary power* (or *molecular rotation*), $[M]$, is given by the formula—

$$\frac{M[\alpha]}{100} = [M] \quad . \quad . \quad . \quad . \quad (14)$$

where M = molecular weight.

The angle through which the plane of polarization of light is rotated by a given substance is dependent upon the wavelength of the light, and to some extent upon the temperature; both these quantities should therefore be stated when reporting data; thus $[\alpha]D^{25}$ indicates a measurement for the D line of sodium made at a temperature of 25°C.

PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

The relationship of physical properties and chemical constitution is a matter of considerable importance in a study of chemistry. The physical properties of systems, mixtures and compounds may be classified into three categories, namely (*a*) additive, (*b*) constitutive, and (*c*) colligative.

Additive properties are those properties which are determined solely by the nature and the number of the atoms or radicals in the molecule. Such properties are not governed by the manner of three-dimensional orientation of atoms or radicals, nor by the manner in which they are combined together. The mass of a molecule is the only property which is strictly additive, but there are other properties (e.g. molecular or molar volume) which are approximately additive.

Constitutive properties depend largely upon the arrangement of the atoms in the molecule, and to a less extent upon their nature and number. There are a number of physical properties which are partly additive, and partly constitutive. Thus for example, refraction is chiefly additive and to a less degree constitutive; whilst boiling point is chiefly determined by the constitutive factor.

Colligative properties are dependent upon the number of molecules present, being independent of their nature. It is, however, in the study of solutions that colligative properties are chiefly encountered and in this connexion are often termed *osmotic* properties. Discussion of these osmotic properties will be considered later. The inter-relationship of a number of physical properties and chemical constitution will now be discussed.

Molecular or Molar Volume. It will be recalled (*see* page 109) that the molecular volume is the volume occupied by one mole of a liquid; expressed mathematically this is

$$\frac{M}{D} = V \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where M = molecular weight of liquid, D = density of liquid, V = molecular volume.

Kopp (1855) pointed out that the molecular volumes of organic compounds measured at their boiling points and under one atmosphere pressure were, to a large degree, additive functions of the volume equivalents of the elements making up the corresponding molecules. It has been shown that in various homologous series there is a constant difference of approximately 22 ml for each increment of a CH_2 group. Since the molecular volumes of butane, C_4H_{10}, and benzene, C_6H_6, are the same, Kopp assumed that the atomic volume of carbon was twice that of the hydrogen atom, therefore,

since $CH_2 = 22$, then $C = 2H = 11$, and $H = 5{\cdot}5$

Utilizing these values it is possible to calculate the atomic volumes of other elements; for example, the molecular volume of diethyl ether $(C_2H_5)_2O$ is found experimentally to be 106·1; calculation of values for the group $(C_2H_5)_2$ gives $4C + 10H = (4 \times 11) + (10 \times 5{\cdot}5) = 99$. Therefore, the atomic value of oxygen is $106{\cdot}1 - 99 = 7{\cdot}1$.

In this manner values may be calculated for the volume equivalents of other elements and these values may be employed to predict the molecular volumes of other substances. This is illustrated by the example of butyl iodide, C_4H_9I.

Butyl Iodide, C_4H_9I

4C = 4 × 11	=	44·0
9H = 9 × 5·5	=	49·5
I = 37·5	=	37·5
V (calculated)	=	131·0
V (observed)	=	128·5

From this example it will be clear that the molecular volume is not simply an additive property, but is affected appreciably by constitutive properties. For example, amongst other factors, the internal pressure is not the same for all liquids, even when at the same temperature, and this introduces irregularities into the values for the molecular volumes.

Allowance for the effect of internal pressure is obtained in the evaluation of the constant called the *parachor* which serves as an index of the comparative or relative volume of a substance. The use of the parachor involves the use of Macleod's equation relating γ, the surface tension of a liquid, to its density, D, and the density of its vapour, d, at the same temperature, thus—

$$\gamma = C(D - d)^4 \text{ or, } \frac{\gamma^{\frac{1}{4}}}{(D - d)} = C \quad . \quad . \quad . \quad (5a)$$

This equation holds over a wide temperature range. If both sides of equation (5a) are multiplied by the molecular weight—

$$\frac{M\gamma^{\frac{1}{4}}}{(D - d)} = \text{a constant termed the "parachor"} \quad . \quad . \quad (16)$$

Since the density of the vapour, d, is usually very small compared with that of the liquid, D, the numerical value of the parachor is approximately equal to the molecular volume multiplied by the fourth root of the surface tension. Thus, if two liquids are examined under such conditions that their surface tensions are equal, then their molecular volumes will be proportional to the values of the parachor.

Sugden has proposed that the molecular parachor is an additive function of the parachors of atoms, linkages and rings, some typical values being quoted in Table 21. The parachors of carbon and hydrogen being fixed first, those of the other elements are evaluated in a similar method to that used for atomic volumes.

TABLE 21

Values for Parachors, Linkages and Rings

Carbon	4·8	Double bond	23·2
Hydrogen	17·1	Triple bond	46·6
Oxygen	20·0	3-membered ring	16·7
Oxygen in esters	60·0	4-membered ring	11·6
Oxygen in hydroxyl	13·3	5-membered ring	8·5
Sulphur	48·5	6-membered ring	6·1
Chlorine	53·8		
Bromine	68·0		
Iodine	90·0		
Nitrogen	12·5		

Thus, employing the values as quoted in Table 21, the value of the molecular parachor for any given molecule may be calculated as the sum of a series of parachor values for the atoms making up the molecule in question. From Table 21 it will be noted that different types of linkage are also given parachor values and by employing these in conjunction with atomic parachors it is possible to elucidate the molecular structures of many compounds.

Optical Properties. As stated on p. 113, the measurement of optical properties is often of considerable value in elucidating molecular structure.

Molecular Refraction. Like molecular volume, this is not strictly simply an additive property but is influenced by constitutive factors. As in the case of parachor values, so also in the case of refraction equivalents, values are apportioned in respect of different types of linkage.

Measurements of refractive index have been used to provide information regarding the molecular structure of many complex organic compounds, particularly as a means of determining the position of double bonds in such compounds.

Optical Rotatary Power. This is dependent upon molecular dissymmetry (dissymmetrical molecules are those which give "non-superposable" images when viewed in a mirror), and thus is wholly a constitutive property. The optical rotatory power of isomeric substances possessing several asymmetric carbon atoms is the algebraic sum of the individual contributions of each separate carbon atom, and is independent of the configurations of the other atoms. This is the principle of *optical superposition* first proposed by van't Hoff.

CHAPTER 7

THE SOLID STATE

THE term *solid* is generally applied to describe those forms of matter exhibiting sufficient rigidity to permit of the maintenance of their characteristic shape. In this respect such substances differ from gases and from liquids. Solids and liquids are similar, however, in that they both possess a definite volume which is only affected to a slight degree by changes of pressure and of temperature.

In scientific terminology at the present time it is usual only to employ the term "solid" in respect of those substances in which the atoms or molecules making up the substance are arranged in a three-dimensional, recurring pattern; such solid substances are said to be *crystalline*. There are, however, a number of apparently solid substances (e.g. glass, pitch and resin) in which the arrangement of atoms or molecules is not regular; such substances are said to be *amorphous*. In respect of their lack of regular atomic or molecular arrangement, amorphous substances are similar to liquids, in fact, glass, pitch and resin are often referred to as *super-cooled* liquids.

It should be noted here that in the amorphous state there is the possibility of some degree of regularity of atomic arrangement, and there appears to be a gradual transition from the condition of perfect regularity of atomic arrangement characteristic of true crystals on the one hand to the condition of a random assembly of atoms on the other hand which is characteristic of non-crystalline substances.

THE CRYSTALLINE STATE

Crystalline solids result when pure liquids are allowed to cool to their freezing points, or when solutions are cooled or are evaporated, or alternatively, when vapours condense under such conditions that the liquid phase is not formed.

By causing the phenomena of cooling, evaporation and condensation to occur slowly it is possible to obtain larger crystals than those obtained during rapid temperature fall.

Many crystalline substances (e.g. rocksalt, calcite, iron pyrites) occur naturally, but it is seldom that such crystals are perfect specimens.

The chief characteristics of crystalline substances are as follows—

(1) They exhibit a definite geometrical form, the same type of substance always crystallizing in the same characteristic form in which the angles

between corresponding faces of different crystals of the same type of substance are constant.

(2) The fracture of crystalline substances, in general, occurs most readily along *cleavage planes* which are inclined to one another at angles which are both constant and characteristic of a given substance.

(3) When pure crystalline substances are heated they melt at a temperature which is definite, reproducible and characteristic of the substance in question.

(4) Certain physical properties of a crystal, such as refractive index, vary according to the direction within the crystal in which the measurement is made.

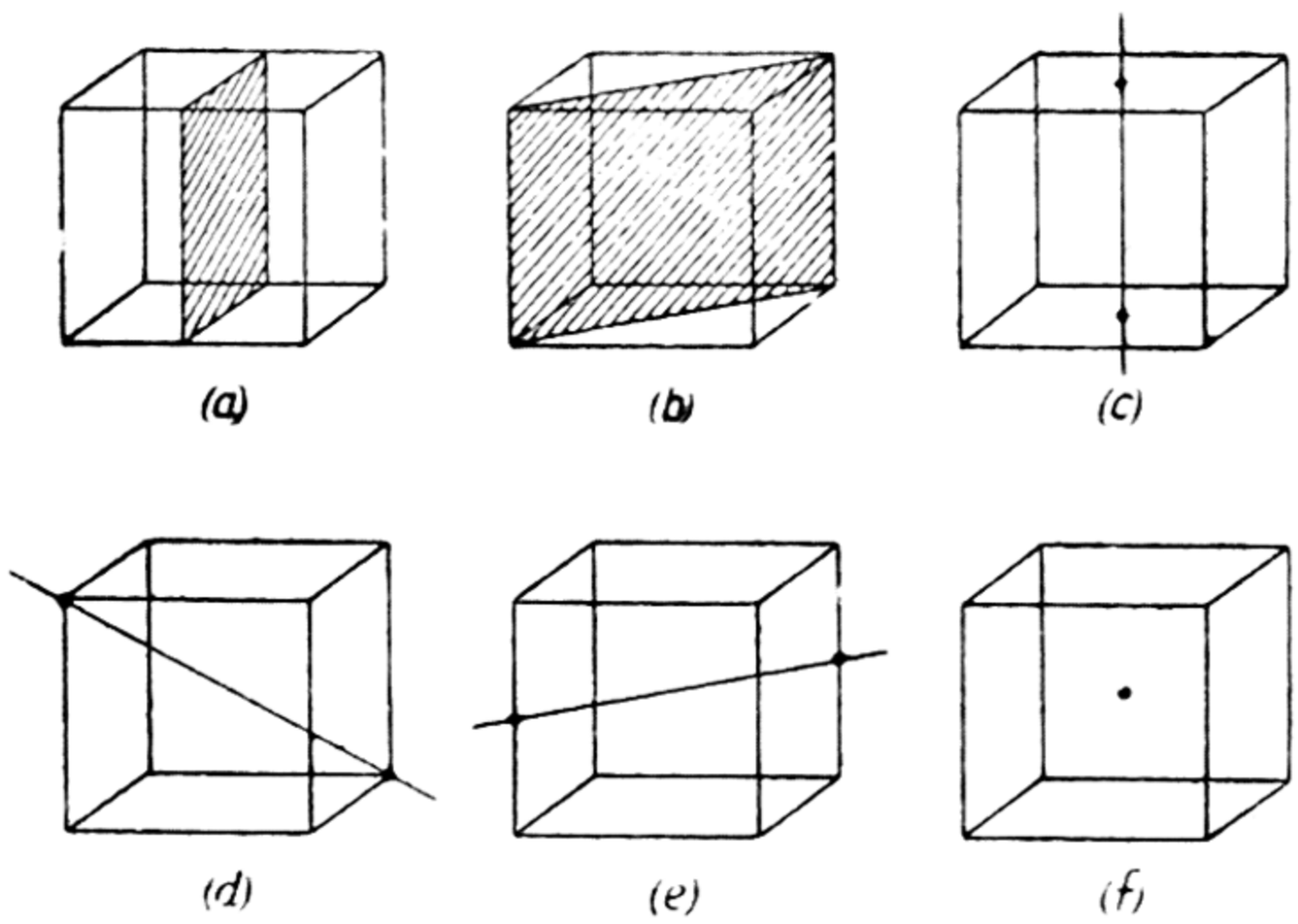


FIG. 35. Crystal Symmetry

(5) Crystalline substances are characterized by their symmetry; on rotating the crystal about an axis, its appearance remains unchanged.

Crystal Symmetry. Three types of crystal symmetry may be distinguished. Firstly, a crystal has a plane of symmetry when it can be divided in the imagination into two parts so that one part is the exact mirror image of the other half (*see* Fig. 35, at (*a*) and (*b*)). Secondly, a crystal possesses an axis of symmetry, that is a line about which, if the crystal be rotated, it will present exactly the same appearance more than once during the course of a complete revolution; thus may be distinguished the two-fold symmetry of a diad axis when this self-coincidence occurs twice during a single revolution, whilst other possibilities are three, four, and six repetitions of the original appearance during a single revolution corresponding to the three-fold (triad), four-fold (tetrad), and six-fold (hexad) axes of symmetry (*see* Fig. 35, at (*c*), (*d*) and (*e*)). Thirdly, a crystal may possess a centre of symmetry, that is, a point within the crystal so that any line drawn through it will intersect the surfaces of the crystal at equal distances on each side of the point (*see* Fig. 35 at (*f*)).

From Fig. 35 it will be observed that the cube possesses a high degree of symmetry, in fact the perfect cube possesses twenty-three elements of symmetry.

Crystallographic Axes. It has already been stated that many naturally occurring substances exhibit a close approach to perfection of external form and for long it was held that such perfection of external form was a pre-requisite of crystallinity. In fact, the systematization of the crystal forms based upon angle-measurements and upon the theory of symmetry was established from a study of such substances.

In 1912, however, Laue, and Friedrich and Knipping, using a method depending on X-ray interference phenomena, were able to obtain experimental proof of the existence of internal symmetry in crystalline substances. Thus has been built up the picture of a crystalline substance as a substance in which the atoms are arranged in a three-dimensional pattern. These atoms exist in sheets or planes, and the points of intersection of these planes constitute the *space lattice* or *crystal lattice*. It is the arrangement of the individual atoms in the space lattice which is responsible for the commonly observed properties of crystals, and as a result of X-ray diffraction analysis the nature of the atomic pattern is revealed and the position of the atoms with respect to one another is rendered capable of determination.

The crystalline pattern is on a scale of 1×10^{-8} cm, and so is far too small to be capable of resolution under the optical microscope, which cannot be employed to resolve the details of a structure on a scale smaller than 1×10^{-4} cm, since it is dependent upon the wavelength of the illuminating beam for its degree of resolution.

Because of the regular arrangement of atoms in crystalline substances it is possible to imagine planes running in different directions throughout the whole mass of the material. On these planes the atoms are more or less densely distributed. The direction of a crystal plane may be defined by reference to a system of axes chosen with respect to the crystal system under consideration. This statement may be illustrated by reference to the cubic lattice, the simplest type of lattice. In Fig. 36, the axes OX, OY and OZ are the intersections of the three principal planes of symmetry; they are perpendicular to one another and of equal length. The broken lines indicate a plane ABC which intersects all the three axes at the same distance from the origin, giving the intercepts or *parameters* OA, OB and OC. The ratios of these intercepts, termed *axial ratios*, are of importance in the description of a crystal. If $OA = a$, $OB = b$, and $OC =$ c, then in quoting the axial ratio it is the convention to write $b = 1$; thus, in the case described above $a : b : c = 1 : 1 : 1$. All faces of the same "form" have the same axial ratios. The angles between the axes YOZ, XOZ and XOY are represented respectively by the symbols, α, β and γ. The actual values for these angles are only quoted if they are other than 90°. The

numerical values for these angles, together with the axial ratios permit of the description of the position of any crystal face being reported. These data constitute what are known as the "elements of a crystal."

If the intercepts of any other crystal faces on the three axes shown in Fig. 36 are measured they will be found to be represented by *la*, *mb* and *nc* where *l*, *m* and *n* are small whole numbers (e.g. 1, 2, 3 and occasionally larger numbers). This is an illustration of the Law of Rational Indices.

In order to represent any particular face, it is customary to make use of *Miller indices*. The Miller indices of a face are inversely proportional to the intercepts of that face on the selected axes. Thus, in Fig. 36, the plane *ABC* cuts off equal intercepts on each of the three axes and so in the Miller

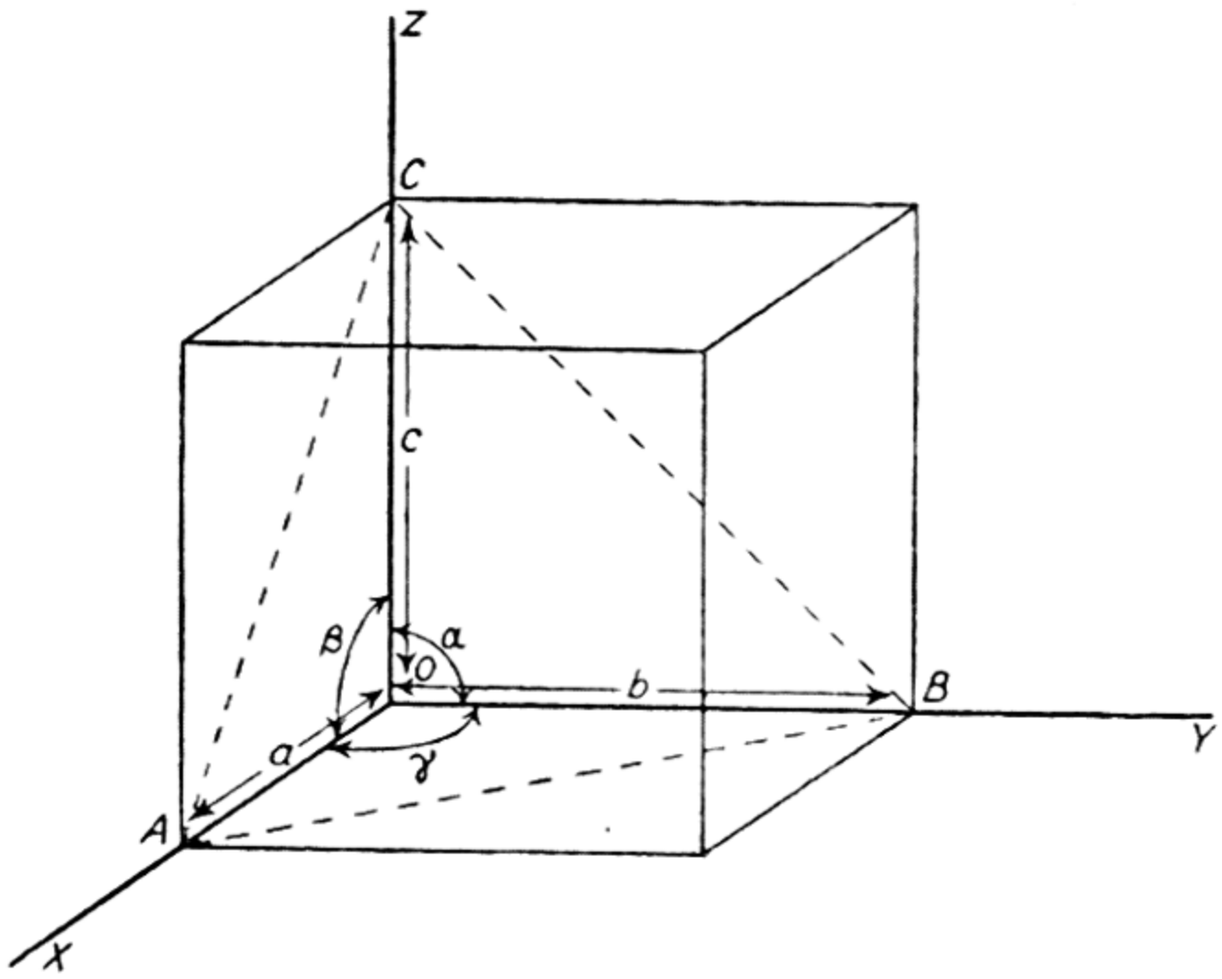


FIG. 36. Crystallographic Axes

system of notation, the indices are (1 1 1), written without commas and enclosed in round brackets. Miller indices are always whole numbers.

The directions *OA*, *OB* and *OC* are all regarded as positive, but directions measured on the other side of the origin are regarded as negative. If the parameters are negative the corresponding index is written with the negative sign above it. For example, if the parameters for a certain plane are $OA = -3$, $OB = 1$ and $OC = 1$, the indices may be thought to be $(\bar{\frac{1}{3}}\ \frac{1}{1}\ \frac{1}{1})$, but since indices express only ratios and *not the actual position of a particular plane*, the indices $(\bar{\frac{1}{3}}\ \frac{1}{1}\ \frac{1}{1})$ are identical crystallographically with $(\bar{1}\ 3\ 3)$ or $(\bar{2}\ 6\ 6)$. The indices $(\bar{1}\ 3\ 3)$ are chosen, since there are no fractions present and because at least one index is unity. Thus, the larger the intercept the smaller the index and vice versa. A particular plane, such as *ABC* (Fig. 36) and the family or form of planes to which it belongs are designated (1 1 1) and {1 1 1} respectively. A direction in a crystal structure is denoted by enclosing the indices within square brackets. Thus is written the [1 1 1] direction.

In Fig. 37 at (*a*) imagine the plane *ABCD* intersecting the plane *OX* at unit distance from the origin. This plane, being parallel to the axes *OY* and *OZ*, can only be regarded as intersecting them at infinite distance. The parameters for this plane are, therefore, 1, ∞, ∞, and the indices (1 0 0). This particular plane is known as the cube face and there are obviously six of these planes in the cubic structure. Similarly, the parameters for the plane *EFHG* (Fig. 37 at (*b*)) are 1, 1, ∞, and the indices (1 1 0). There are six sets of the {1 1 0} form of planes.

Crystallographic Systems. By means of the geometrical considerations outlined above it has been shown that thirty-two classes of crystal symmetry or "point groups" are possible. These thirty-two different classes may be arranged in seven systems, each system being characterized by its own axial angles and axial ratios. Six of the systems may be represented

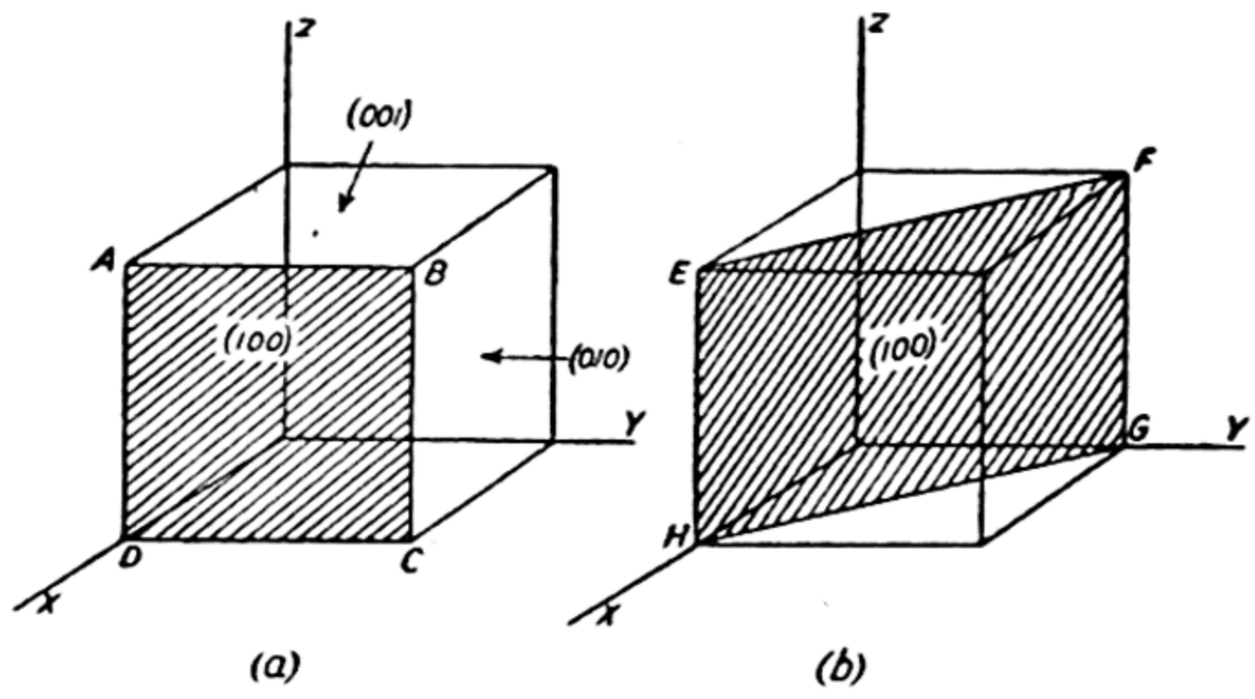


FIG. 37. Miller Indices

by three crystallographic axes, but the seventh, the hexagonal system, is referred to a set of four axes. The chief characteristics of these seven systems are tabulated in Table 22.

When a crystalline substance exhibits a property to some degree, no matter in which direction within the crystal that property be measured, then such a crystalline substance is said to be *isotropic*. This state of affairs obtains in cubic crystals since they have the same structure in all directions. Crystals in other systems are however, *anisotropic* in that a property will not have the same magnitude if measured in different directions. Thus, for example, Iceland Spar markedly exhibits the phenomenon of double refraction, which incidentally may be detected in all crystals other than those in the cubic system.

Types of Crystal Structure

In a crystal the atomic pattern is repeated in three dimensions throughout the whole mass of the material, the unit of repetition being known as the "unit cell." The position of the centres of the atoms is frequently that corresponding to the closest packing of spheres. If the first layer of atoms

TABLE 22

Crystallographic Systems

System	Crystallographic Elements	Essential Symmetry
Cubic or Regular . .	Three axes at right angles: all equal— $\alpha = \beta = \gamma = 90°$ $a:b:c = 1:1:1$	4 triad axes, 3 diad or 3 tetrad axes
Tetragonal . . .	Three axes at right angles: two equal— $\alpha = \beta = \gamma = 90°$ $a:b:c = 1:1:y$	1 tetrad axis
Orthorhombic or Rhombic .	Three axes at right angles: unequal— $\alpha = \beta = \gamma = 90°$ $a:b:c = x:1:y$	3 diad axes, or 1 diad axis and 2 perpendicular planes intersecting in a diad axis
Monoclinic . . .	Three axes, one pair not at right angles: unequal— $\alpha = \gamma = 90° : \beta \neq 90°$ $a:b:c = x:1:y$	1 diad axis or 1 plane
Triclinic or Anorthic . .	Three axes not at right angles: unequal— $\alpha, \beta, \gamma \neq 90°$ $a:b:c = x:1:y$	No axes or planes
Rhombohedral or Trigonal.	Three axes equally inclined, not at right angles: all equal— $\alpha = \beta = \gamma \neq 90°$ $a:b:c = 1:1:1$	1 triad axis
Hexagonal . . .	Three axes coplanar at 60°: equal. Fourth axis at right angles to other three— $a_1:a_2:a_3:b = 1:1:1:x$	1 hexad axis

is represented by spheres of equal size so placed that they just touch one another (Fig. 38) it will be noted that the lines connecting the centres of each three adjacent spheres form a series of equilaterial triangles, and the centres of seven adjacent spheres a centred hexagon of seven spheres. A second layer may be placed upon this base layer, each sphere of the second

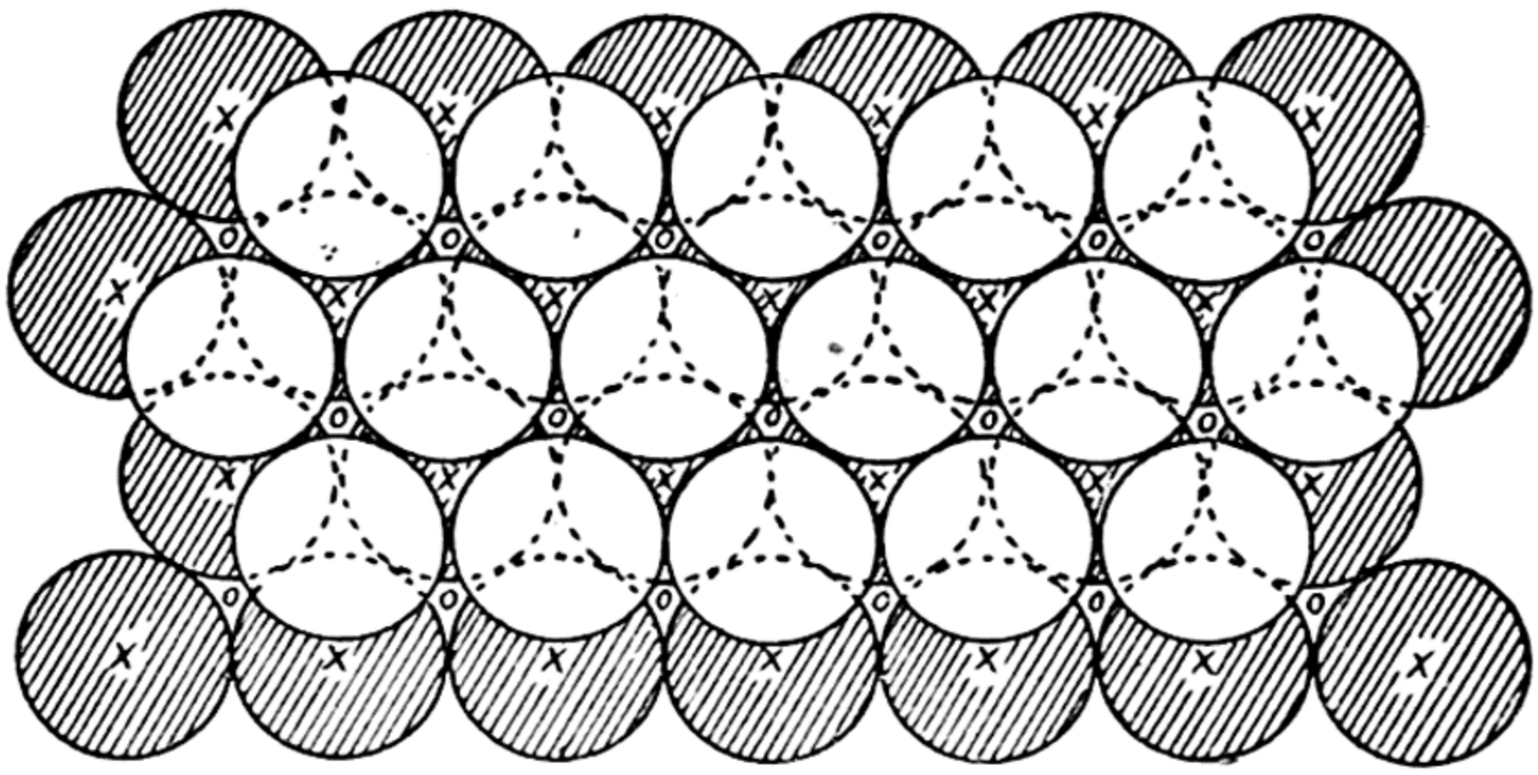


FIG. 38. Closest Packing of Spheres

layer lying in the hollow between two adjacent spheres of the base layer. It should be carefully noted that only every *alternate triangle* of the base layer can be loaded in this way. The third layer may be laid down in one of two ways, either—

(*a*) Each third-layer sphere may be laid over the centre of every sphere in the base layer. The centres of the third-layer spheres are indicated in

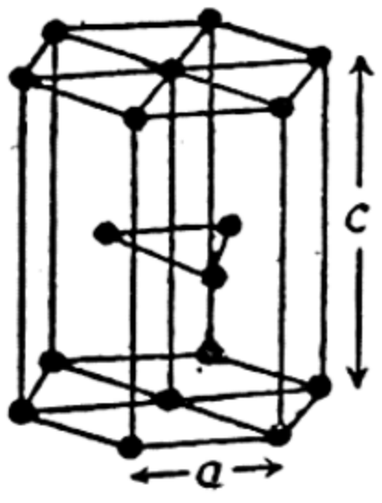


FIG. 39. Hexagonal Close-packed Structure

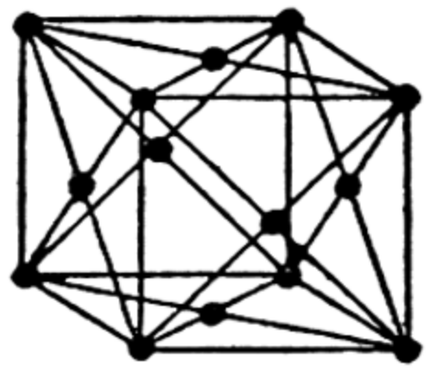


FIG. 40. Face-centred Cubic Structure

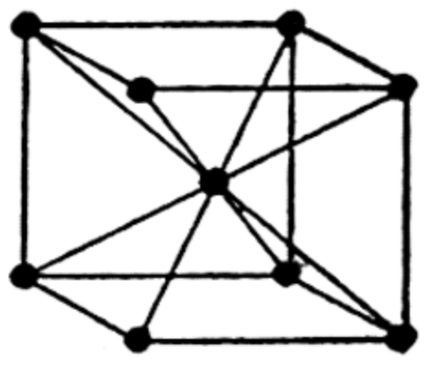


FIG. 41. Body-centred Cubic Structure

Fig. 38 by the letter *x*. This method of assembly is termed the "hexagonal close-packed" structure. It is represented diagrammatically in Fig. 39 where each black sphere represents an atom. It should be carefully noted that in diagrams such as Fig. 39, atoms are represented for purposes of clarity by a small sphere whereas in actual fact the atoms are almost in contact with very little free space between them.

(*b*) Each third-layer sphere may be laid over the centres of the triangles *which were skipped when laying the second layer*. The centres of the third-layer spheres in this arrangement are indicated by the letter *o*. This

arrangement is termed the "face-centred" cubic structure and is shown diagrammatically in Fig. 40.

Atoms, however, frequently take up positions which do not correspond with the closest packing of spheres, one such arrangement being the "body-centred" cubic structure in which the atoms occupy the corners and the centre of the unit cube. The unit cell of this type of structure is shown in Fig. 41. Comparison of Figs. 40 and 41 will indicate how open is the body-centred cubic structure compared with the face-centred cubic structure.

For the closest packing to occur in the hexagonal close-packed structure, the ratio of the height, *c*, Fig. 39, to the length of one of the sides of the base, *a*, must be 1·633. This ratio is termed the *axial ratio*.

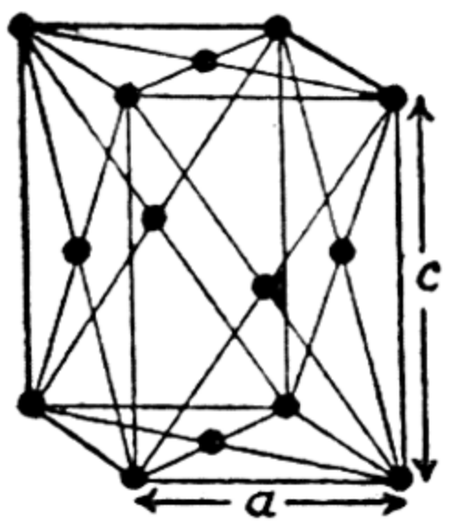


FIG. 42. Face-centred Tetragonal Structure

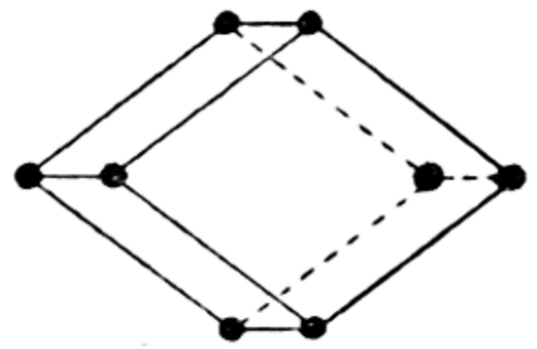


FIG. 43. Rhombohedral Structure

Two other types of crystal structure are the face-centred tetragonal structure (Fig. 42), which resembles the face-centred cubic lattice except that one axis is longer than the other two, and the rhombohedral structure (Fig. 43) in which one atom has three close neighbours, three other atoms being at a slightly greater distance.

Results of Crystal Structure Measurements

Non-metallic Elements. These elements are characterized by the fact that each atom is joined by a covalent bond to one or more neighbouring atoms, the actual number being the same as the usual valency value for the element in question.

The element carbon, in the form of diamond, possesses a structure in which each carbon atom is surrounded by four other carbon atoms situated at the corners of a regular tetrahedron (*see* Fig. 44 at (*a*)). In graphite, however, the carbon atoms are arranged in the form of flat sheets in each of which the carbon atoms, joined by covalent bonds, exist in flat hexagons (*see* Fig. 44 at (*b*)). The distance between the adjoining sheets is too large to correspond to a chemical bond so that in any one sheet each carbon atom is attached to only three neighbouring atoms instead of to four, as in the case of the diamond structure. Substances,

such as graphite, consisting of sheets of atoms which are separated by distances too great to permit of chemical bonding are said to have "layer lattices."

Metallic Elements. The great majority of the metallic elements crystallize in face-centred cubic, body-centred cubic, and hexagonal close-packed structures. Metal atoms cannot be held together by ordinary covalent bonds since the number of electrons available is insufficient. Nevertheless, metals exhibit considerable strength and it has been suggested that a special type of bond, the so-called *metallic bond*, characterizes the metals in which a relatively small number of electrons is able to bind together a

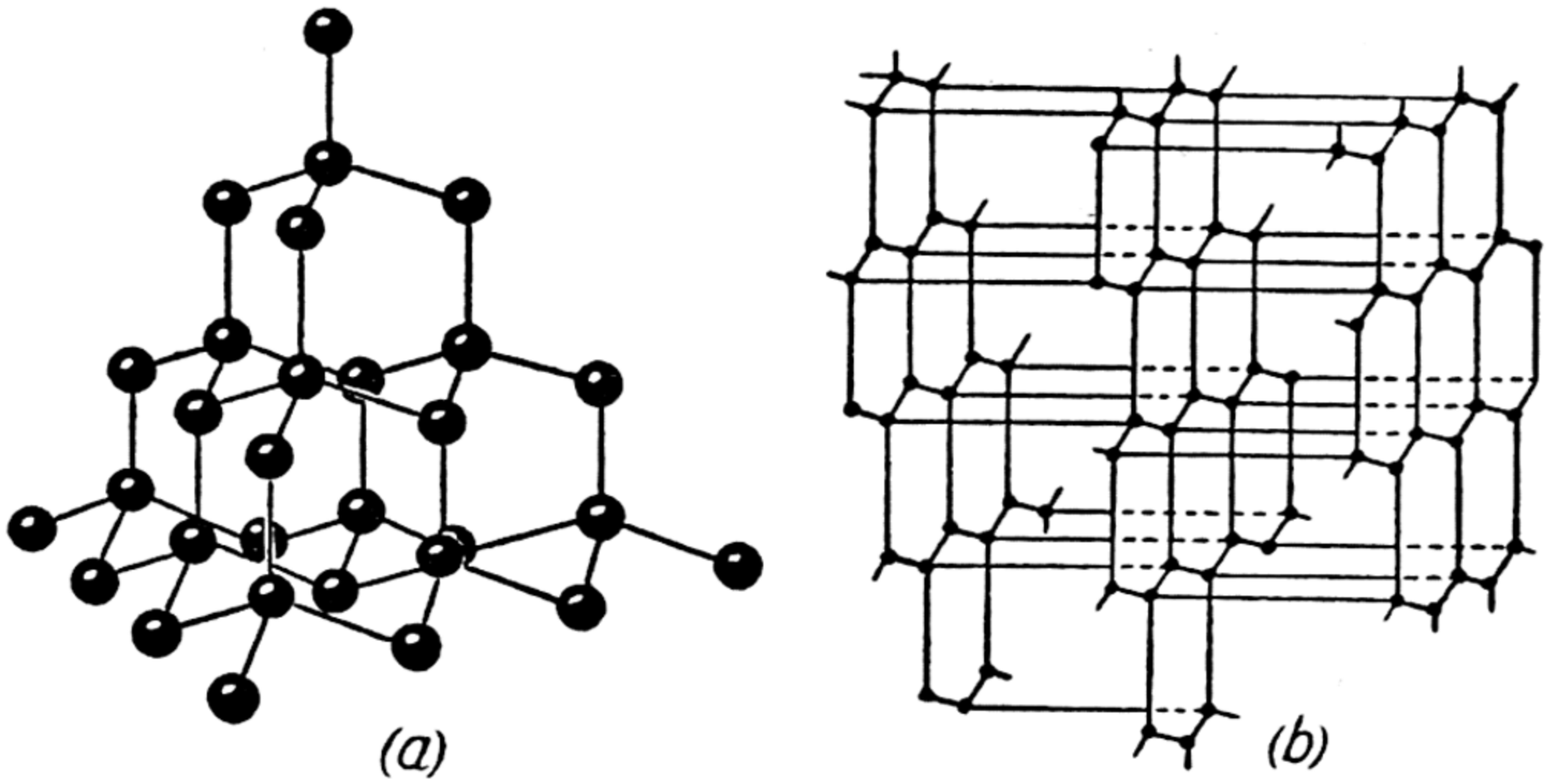


FIG. 44. (*a*) Diamond Structure, (*b*) Graphite Structure

larger number of ions, the valency electrons thus constituting a mobile lattice.

Inorganic Compounds. The structure of a large number of inorganic compounds has been elucidated by means of X-ray diffraction analysis. Thus, in sodium chloride the atoms, or more correctly the ions, are arranged in the form of a lattice as is depicted in Fig. 45 (*a*). It is due to the existence of the charges resident upon the individual ions that the sodium and chlorine ions are held rigidly in place.

It does not follow, however, that the radius of the sodium ion in sodium chloride is the same as that in sodium iodide, since the different atomic volume and the greater number of electrons in iodine as compared with chlorine cause an alteration in the volume available to the sodium.

In addition, it does not necessarily follow that caesium chloride and sodium chloride will exhibit the same type of crystal structure even though these two metals occur in the same group of the Periodic Classification; this will be evident from Fig. 45 (*a*) and (*b*). All the alkali metal halides (except the chloride, bromide and iodide of caesium), and many oxides

and sulphides have the same crystal structure as Fig. 45 (*a*) and are, therefore, said to have the "sodium chloride" structure.

The body-centred cubic structure of caesium chloride is also possessed by the halides of thallium and ammonium.

These examples will indicate the general nature of atomic arrangement in some of the simpler crystals, although it should be carefully noted that not all binary compounds crystallize in the cubic system.

In the correlation of crystal structure with physical properties a number of factors are involved and the problem is far from simple. However, it may be stated that, in general, with increasing distance between neighbouring atomic centres in *ionic* crystals there is a corresponding decrease in

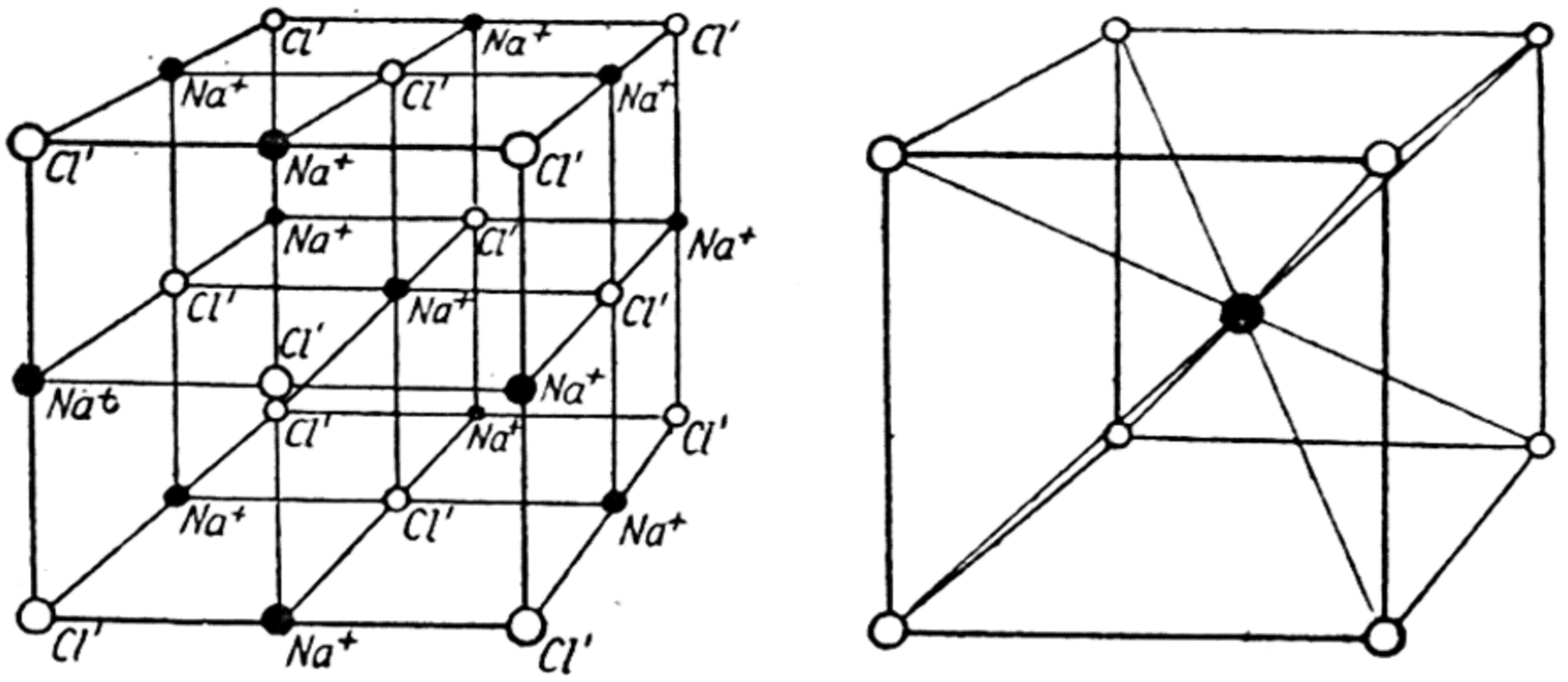


FIG. 45. (*a*) Sodium Chloride Structure, (*b*) Caesium Chloride Structure

hardness, and a fall in melting point. A number of inorganic crystals are not of the ionic type but consist of atoms; this is especially true of crystals of intermetallic compounds which possess bonds similar to those found in crystals of a metallic element. X-ray diffraction analysis has been particularly valuable in helping to elucidate the structure of complex compounds such as the silicates, and co-ordination compounds.

Organic Compounds. The crystal structure of a considerable number of organic compounds has been determined by X-ray diffraction analysis. Thus, it has been shown that the fatty acids are made up of long chains packed side by side in the crystal, the whole structure being made up of a number of such layers arranged one on the other, these chains being oriented perpendicularly, or nearly perpendicularly, to the plane of the sheets.

The planar, regular hexagonal structure of the benzene ring has been established from X-ray diffraction measurements, and, in addition, the detailed structure of many other aromatic compounds elucidated. X-ray diffraction analysis has also been applied to fibrous materials such as cellulose, the proteins, rubber and artificial long chain polymers.

Determination of the Avogadro Number. Using a crystal of known

structure, the size of a unit cell, as determined from X-ray diffraction measurements, may be employed to evaluate the Avogadro Number. Thus taking sodium chloride as an example, the unit cube contains four sodium ions and four chlorine ions. Resulting from X-ray diffraction analysis the length of the cube edge is $5{\cdot}638 \times 10^{-8}$ cm and the volume of the unit cube is $(5{\cdot}638 \times 10^{-8})^3$ cm^3. Since the density of sodium chloride is 2·163 the volume occupied by four gramme atoms of each element is $4(23{\cdot}0 - 35{\cdot}46)/2{\cdot}163 = 108{\cdot}1$ cm^3 and the ratio of the volume of four gramme molecules of sodium chloride to four *molecules* of this compound is $108{\cdot}1/(5{\cdot}638 \times 10^{-8})^3 = 6{\cdot}03 \times 10^{23}$.

Isomorphism

It is often found that the corresponding compounds of chemically similar elements form crystals exhibiting a close resemblance, except in respect of their colour. This phenomenon is termed *isomorphism*, and the compounds concerned are said to be *isomorphous*.

One of the best examples of isomorphism is to be found in the group of compounds known as the alums (*see* p. 551). The general formula for the alums is—

$$X_2SO_4 \,.\, Y_2(SO_4)_3 \,.\, 24H_2O$$

where X is one of the univalent alkali metals, or thallium or the radical, ammonium, and *Y* is one of the trivalent metals, aluminium, iron, chromium, gallium, indium, titanium, vanadium, cobalt, manganese, rhodium, iridium.

The colourless, octahedral crystals of potash alum, $K_2SO_4 \,.\, Al_2(SO_4)_3 \,.\, 24H_2O$ are closely similar in external form to the violet, octahedral crystals of chrome alum, $K_2SO_4 \,.\, Cr_2(SO_3)_4 \,.\, 24H_2O$. This similarity of crystalline form is emphasized by the fact that if a crystal of chrome alum is suspended in a solution of potash alum the colourless potash alum will crystallize in layers parallel to the faces of the chrome alum. The alums thus possess the ability to form *overgrowths*. Similarly, if a solution of two isomorphous salts (e.g. a mixture of two alums, or a mixture of a phosphate and an arsenate) is allowed to crystallize, the resulting crystals are homogeneous in composition containing both substances in the ratio of their relative proportions in the initial solution. Such homogeneous solids are known as *solid solutions*. Sometimes the term "mixed crystals" has been employed instead of the "solid solution," but the latter term is to be preferred since the solid which crystallizes out is a true homogeneous solution of one substance in another, and has many of the properties of a solution.

Solid solutions occur frequently in metallic alloys the properties of which substances they influence considerably.

The phenomenon of isomorphism was first observed by Mitscherlich who concluded that *substances which are similar in crystalline form and in*

chemical properties may usually be represented by similar chemical formulae; this statement is known as Mitscherlich's Law of Isomorphism.

Polymorphism

Many substances are capable of existence in more than one crystalline form; this phenomenon, known as *polymorphism*, occurs in a large number of substances of widely differing characteristics, both elements and compounds, inorganic and organic, and such substances are termed *dimorphic*, *trimorphic* and so on, according as there may be two, three or more forms capable of separate existence.

When polymorphism is exhibited by an element this phenomenon is usually termed *allotropy*. Should each of two forms of a polymorphic substance be isomorphous with a form of another polymorphic substance this phenomenon is known as *isopolymorphism*. Thus, arsenic trioxide and antimony trioxide are isodimorphous, whilst stannic oxide and titanium dioxide are isotrimorphous.

Three types of allotropy are distinguished, namely monotropy, enantiotropy, and dynamic allotropy. In the case of monotropy only one allotropic modification exhibits stability under normal conditions, other modifications being unstable (i.e. metastable) and tending to transform into the stable form. Examples of monotropy are provided by carbon in which case graphite is the stable form, the metastable form being the diamond; and by phosphorus where red phosphorus is the stable form and yellow phosphorus the metastable form. Thus, this polymorphic change can only take place in one direction, that is from the metastable form to the stable form.

In the case of enantiotropy each allotrope of the substance is only capable of stable existence over a specific temperature range. The temperature at which one allotropic form transforms into another form is known as the *transition temperature* or *transition point*. At the transition point the change from one form to the other may occur in either direction; it is a reversible transformation, and only at the transition point can the two forms co-exist. Examples of enantiotropy are provided by rhombic and monoclinic sulphur, and grey and white tin.

In dynamic allotropy the allotropes of a substance are capable of coexistence and possess stability over a wide range of physical conditions, variation of physical conditions within this range causing a change in the proportions of the different allotropes. One of the simplest examples of dynamic allotropy is provided by iodine vapour. There are two allotropes, the monatomic molecule, I, and the diatomic molecule, I_2, and as the temperature is varied so the proportions of these two allotropes also vary; thus, at 500°C, there are no monatomic molecules present, but as the temperature progressivley rises, so the proportion of these molecules increases, being 40 per cent at 1000°C, and 85 per cent at 1500°C.

Diffusion in the Solid State

It has been shown above that crystalline solids consist of a three dimensional recurring array with either atoms or ions occupying fixed points in the space lattice. Although each ion (or each atom) may still oscillate about a mean position, it does not possess the same freedom of movement as when the substance it composes was in either the liquid or the gaseous states. Nevertheless, in spite of such relative fixity of position it is possible for any ion (or atom), by virtue of collision with its neighbours, to attain a velocity sufficient to cause its movement to some other position in the space lattice, with the result that its original position will be occupied by some other ion or atom. In this manner a very slow diffusion in the solid state may occur.

The simplest possible condition of such diffusion is that of "self-diffusion," in which there occurs a migration of atoms in a solid, composed entirely of the same kind of atoms, by a simple exchange of position. Hevesy studied such a phenomenon by measuring the diffusion of thorium B, a radioactive isotope of lead, through ordinary lead. The use of a radioactive isotope in this manner amounts, more or less, to the attaching of labels to atoms in order that they may be readily identified on arrival at their destination.

In general, for atoms of similar size, diffusion through a space lattice implies that the diffusing element is capable of entering into solid solution with the "solvent" element. If such solid solubility is unattainable then diffusion in the solid state is confined to the grain boundaries, due possibly to a disturbance of the lattice in these regions. These statements are in line with the findings of Hevesy who noted that with increasing reduction in the grain size, the more rapid was the rate of diffusion, whilst in the case of a single crystal of lead diffusion was imperceptible.

At any given temperature, atoms which form interstitial solid solutions (e.g. carbon and nitrogen in iron) in general exhibit rates of diffusion greater than those of atoms which form substitutional solid solutions.

This phenomenon of diffusion in the solid state is of very great technical importance and constitutes the underlying basis of such metallurgical processes as carburizing, or cementation (diffusion of carbon into iron), calorizing (diffusion of aluminium into iron), sheradizing (diffusion of zinc into iron), nitriding (diffusion of nitrogen into alloy steel), chromizing (diffusion of chromium into iron). Diffusion in the solid state may also give rise to the production of metallurgical faults as when at an exceedingly high temperature nitrogen diffuses into plain carbon steel during arc welding; thus a weld brittleness or "rottenness" results.

It should be noted that after diffusion has occurred, intermetallic compounds are often formed, for example, iron carbide (cementite) is produced during the processes of carburizing and cementation.

Specific Heats of Solid

As explained above, the atoms or ions in a solid are never at rest but at all temperatures—even at the absolute zero—exist in a condition of vibration about certain mean equilibrium positions. As the temperature rises the amplitude of vibration increases and hence also the mean potential and kinetic energies. It is the *rate* of increase of the vibrational energy with temperature which determines the specific heat of solids. It will be recalled that the "law" of Dulong and Petit states that "most solid elements have the same atomic heats." This "law" is however inexact as is evident from Table 23.

TABLE 23

Atomic Heats of Solid Elements
(*at constant pressure and* 20°*C*)

Element	Atomic Weight	Specific Heat	Atomic Heat
Lithium . . .	7	0·92	6·4 cal
Aluminium . . .	27	0·21	5·7
Calcium . . .	40	0·15	6·0
Iron . . .	56	0·11	6·2
Arsenic . . .	75	0·083	6·2
Silver . . .	108	0·056	6·0
Iodine	127	0·052	6·6
Tantalum . . .	181	0·033	5·9
Mercury . .	200	0·033	6·6
Uranium . . .	238	0·027	6·4

Research in recent years has shown that the atomic heats of all solid elements approach zero at absolute zero, but at elevated temperatures—which are different for differing elements—the atomic heat increases to a constant value. This will be evident from Fig. 46.

The work of Dulong and Petit has been extended by many workers, notably by Joule and by Kopp. The latter worker has proposed the generalization that *the molecular heat of a solid compound is approximately equal to the sum of the atomic heats of its constituents;* this statement is usually known as Kopp's Law.

Vapour Pressures of Solids

A solid, like a liquid, exhibits a specific vapour pressure at any one temperature. There are certain exceptions to this generalization; for example, helium, when below its critical point, cannot exist in contact

with its vapour. Provided that the vapour pressure of a solid is of sufficient magnitude it may be measured by the direct static method but in general this method is not normally applied because of the relatively low vapour pressures experienced; methods involving either transpiration or determination of loss of weight in vacuum are more usually employed. The principles involved are the same as those encountered in the measurement of the vapour pressure of liquids (*see* p. 104).

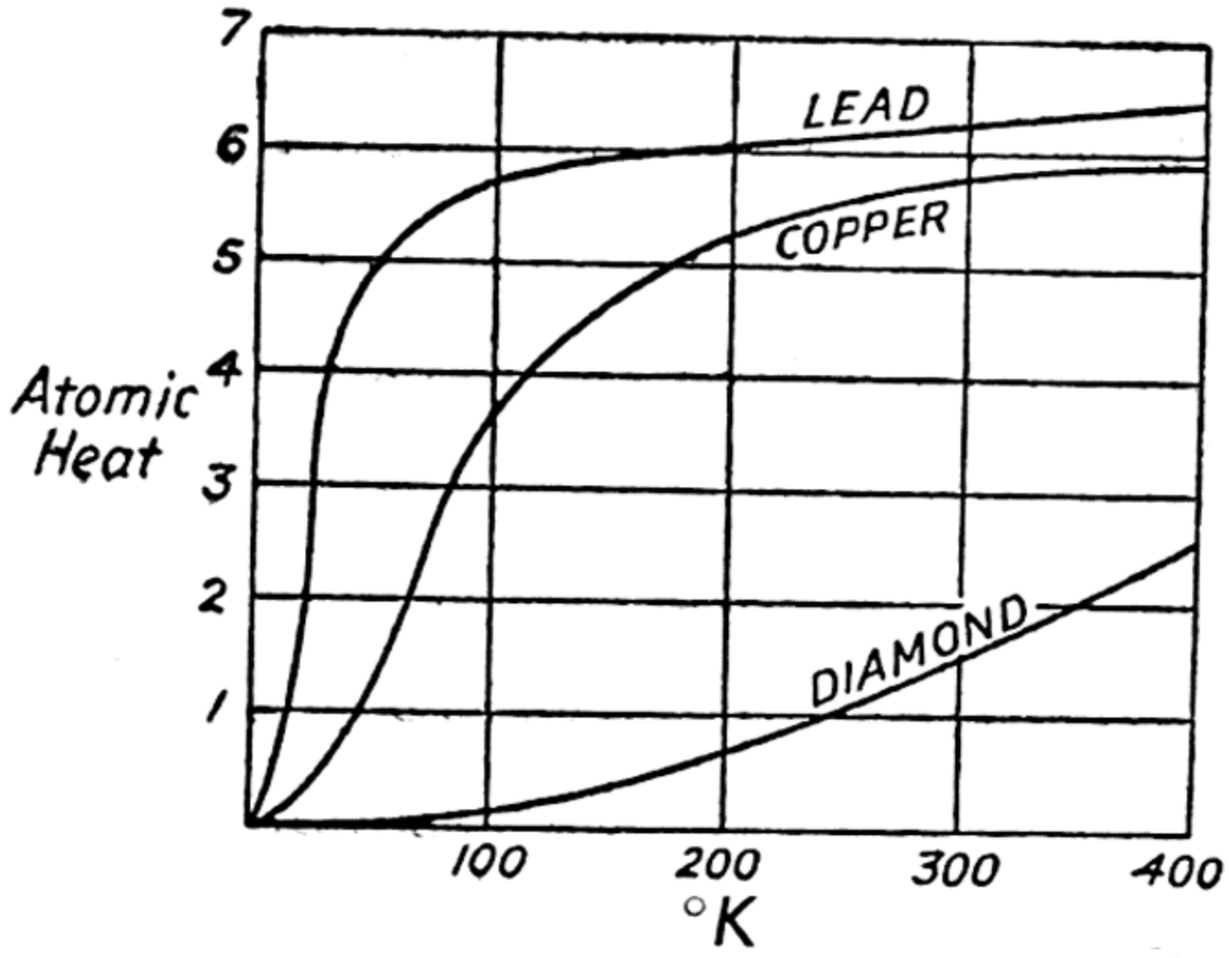


FIG. 46. Variation with Temperature of Atomic Heat

The direct conversion of solid to vapour without the production of liquid is known as *sublimation*. The vapour pressure of a solid increases with rising temperature and may be depicted by the so-called "sublimation curve" which is similar in type to that for the variation of the vapour pressure of a liquid with rising temperature (*see* Fig. 32).

Fusion of Solids

When heat is applied to a pure crystalline solid a temperature is ultimately attained at which the solid changes suddenly to a liquid; this temperature is the *melting point*. On cooling, the liquid will undergo solidification at precisely the same temperature provided that the pressure is maintained constant. In general, the effect of variation of pressure on the melting point of a crystalline solid is very small indeed; for example, an increase of 1000 atmospheres changes the melting point of ice by less than 1°C. The heat absorbed by the melting of a solid to liquid at the melting point is termed the *latent heat of fusion*.

CHAPTER 8

DILUTE SOLUTIONS AND THEIR COLLIGATIVE PROPERTIES

A SOLUTION is a homogeneous mixture of two or more separate, component substances in a condition of molecular dispersion. The term "solution" is capable of very wide interpretation since both *solvent*—the substance present in excess—and *solute*—the dissolved substance—may exist in the gaseous, the liquid, and the solid states. Air is a gaseous solution of nitrogen, oxygen, carbon dioxide and the inert gases; soda water is a liquid solution of carbon dioxide and water, whilst the alloy known as brass is a solid solution of copper and zinc. It should be noted that the component substances from which a solution is made up are not interconvertible by physical methods.

For the purpose of the present discussion it will be assumed that whilst the solvent is volatile, the solute is non-volatile. In the present chapter it is the intention, therefore, to discuss some of the more important properties of liquid solutions which are dependent chiefly upon the number, and not upon the nature of the molecules present. Such properties are usually termed *colligative properties*, although they are sometimes referred to as *osmotic properties*. The specific properties to be discussed are the lowering of the vapour pressure, the elevation of the boiling point, the depression of the freezing point, and the osmotic pressure of solutions.

CONCENTRATION OF SOLUTIONS

The concentration of a solution may be expressed in a number of ways, each way having its own usefulness. Often the concentration is expressed as the number of grammes of solute per 100 g of solvent or the number of grammes of solute per litre of solution.

It is sometimes more useful to quote the number of gramme molecular weights (gramme formula weights) or "moles" per litre of solution; thus may be quoted the *molarity* of a solution. In analytical chemistry great use is made of the so-called normality of a solution, that is the number of gramme equivalent weights of the solute per litre of solution.

For certain purposes it is more convenient to report the concentration of a solution in terms of *molality*, that is the number of gramme molecular weights (moles) per 1000 g of solvent. Sometimes the concentrations of the components of a solution are described in terms of their *mol fractions*. The mol fraction of a component is the ratio of the number of moles of that component to the total number of moles present. The sum of the mol

fractions of all the component substances in any given solution is thus equal to unity.

A *saturated solution* at a specified temperature is a solution which is in equilibrium with undissolved solute. By the evaporation or the cooling of a solution the solubility of a solute may often be exceeded, and the solution then attains the metastable state of *supersaturation* and is a supersaturated solution. Deposition of the amount of solute in excess of solubility

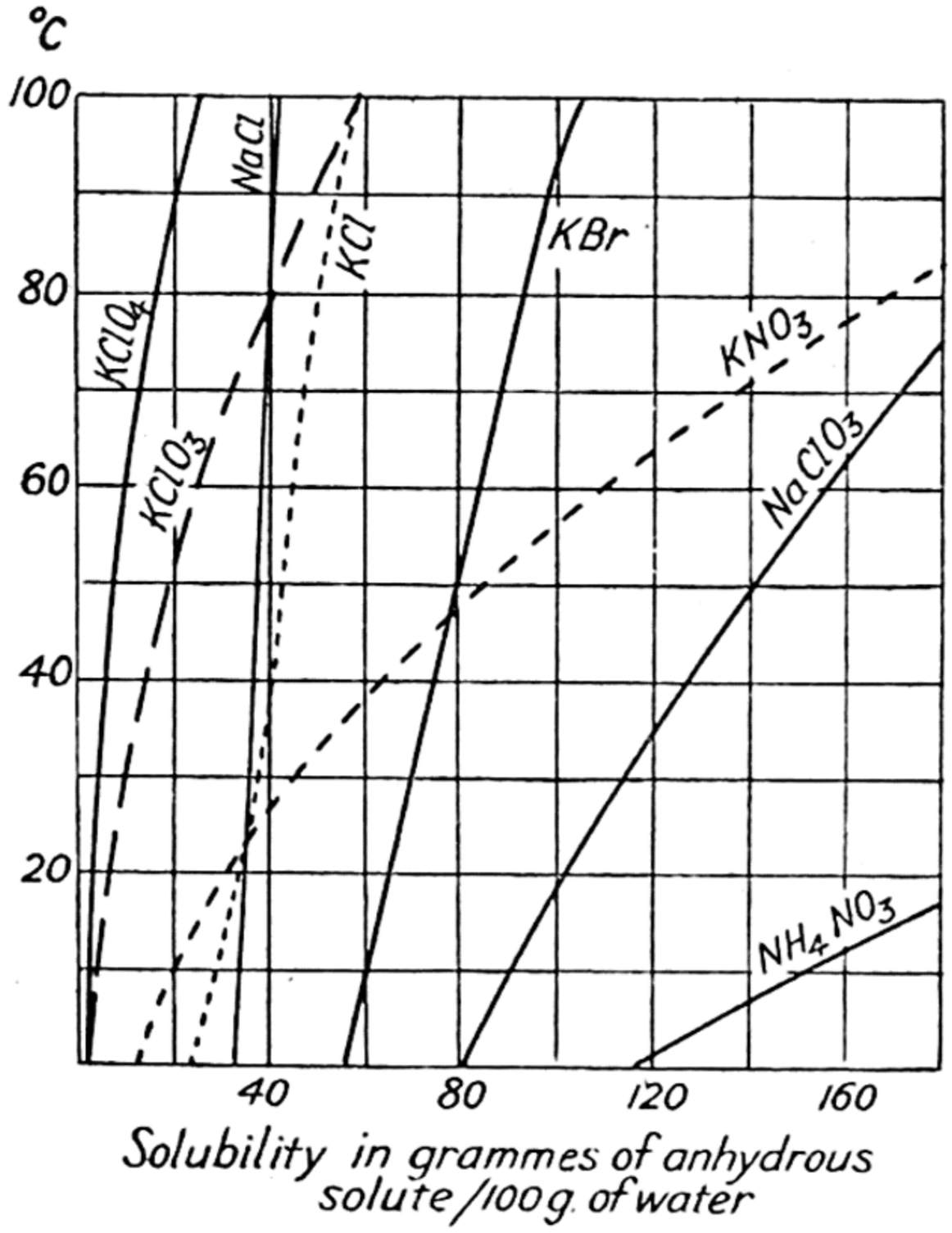


FIG. 47. Solubility Curves for some Salts in Water

requirements may be brought about by stirring, or by shaking the solution, or, alternatively, by introducing into the solution a crystal of the solute (or of some substance isomorphous with it). This latter process which is termed *seeding* or *inoculation* results in the growth of the crystalline solute on top of the crystal introduced.

Effect of Temperature Variation upon Solubility

Although the solubility of most substances at constant pressure increases with rising temperature, the solubility of some substances decreases with rising temperature, whilst in the case of a few substances the solubility increases at the lower end of the temperature scale, but falls at higher temperatures. These phenomena are related to the fact that the process of solution is always associated with either the evolution or the absorption

of heat. Those solutes which evolve heat on dissolving (i.e. with a positive heat of solution) exhibit a decreasing solubility with rising temperature; the reverse holds for those solutes with a negative heat of solution. Most solutes belong to the latter group being more soluble in the hot solvent. These generalizations are a consequence of Le Chatelier's Principle (*see* p. 224); thus, if a system, made up of solvent and solute, exists in equilibrium at a specific temperature and the temperature is raised, the equilibrium will move in such a direction as will tend to restore the system to its initial temperature. This shift of equilibrium will involve more solute

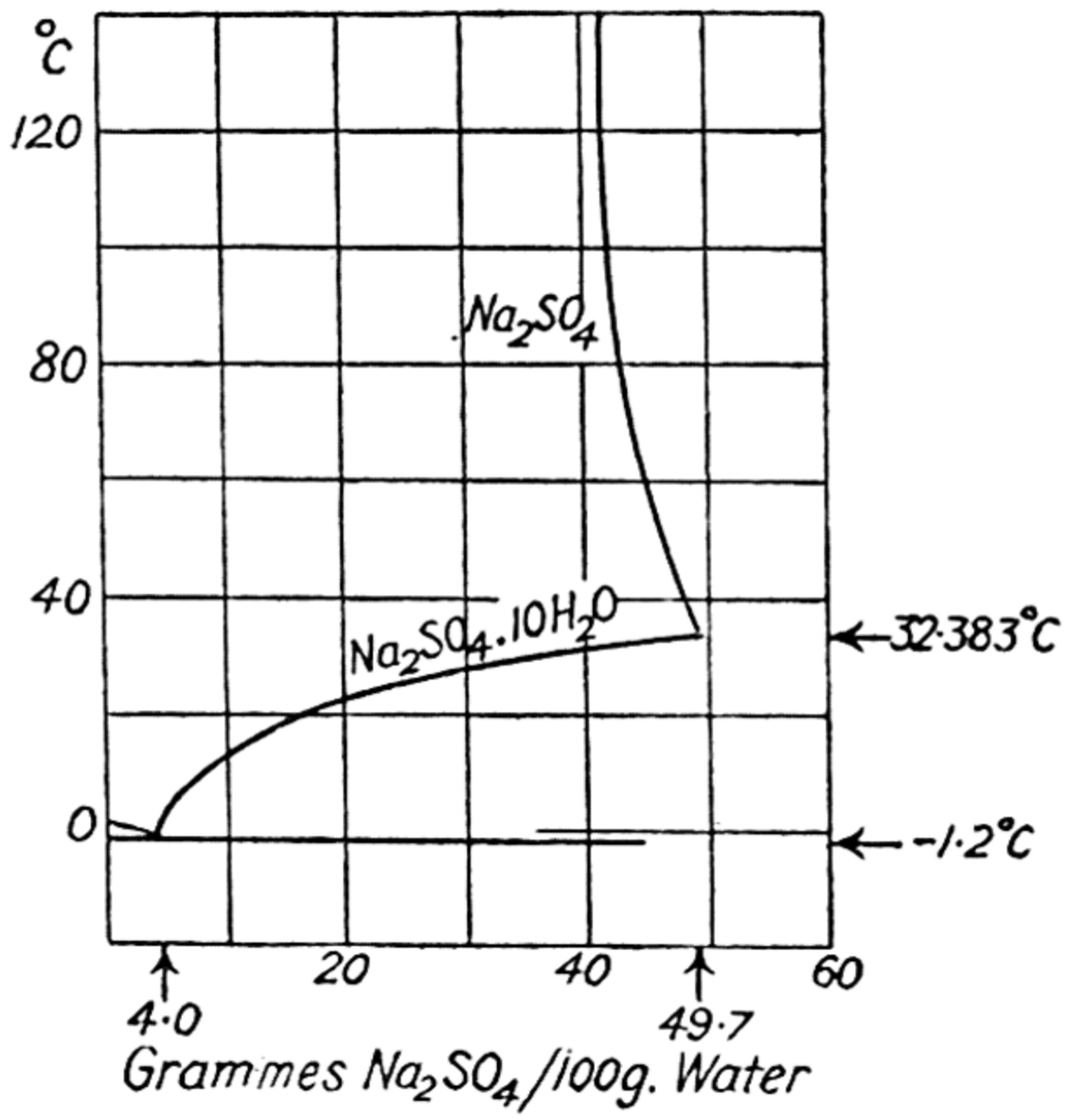


FIG. 48. Equilibrium Diagram for the System Sodium Sulphate-Water

dissolving if the heat of solution is negative, and solute leaving the solution should the heat of solution be positive. The relationship of solubility and temperature is usually depicted graphically, some typical examples of solubility curves being included in Fig. 47.

An example of a solubility curve which exhibits a sudden change of direction with variation of temperature is provided by sodium sulphate. From Fig. 48 it will be noted that the solubility of sodium sulphate decahydrate, $Na_2SO_4 . 10H_2O$ (the stable phase below 32·383°C) increases very rapidly with rising temperature. Above 32·383°C, the stable phase is anhydrous sodium sulphate, Na_2SO_4, the solubility of this phase decreasing with rising temperature.

The Solubility of Salts and Hydroxides

It is often of value to know the approximate solubility of common substances in water.

In the following generalizations on solubility, reference is made only to compounds of the elements listed below.

Sodium, potassium and ammonium.
Magnesium, calcium, strontium and barium.
Aluminium.
Chromium.
Manganese.
Iron (Fe^{++} and Fe^{+++}), cobalt and nickel.
Copper and silver.
Zinc, cadmium and mercury (Hg^{+} and Hg^{++}).
Tin and lead.

In Table 24 the term "soluble" refers to substances with solubility in excess of approximately 1 g/100 ml; the term "insoluble" implies that the solubility is less than about 0·1 g/100 ml; whilst for substances with solubilities lying between, or close to these limits the term "sparingly soluble" is used.

Lowering of Vapour Pressure

It has long been known that when a volatile solute is dissolved in a volatile solvent the vapour pressure of the solvent is lowered. The first quantitative work on vapour pressure of solutions was carried out by von Babo (1847) who, after measuring the vapour pressure of aqueous salt solutions at various temperatures, concluded that if p_0 is the vapour pressure of the pure solvent, and p the vapour pressure of the solution, then for any given solution—

$$\frac{(p_0 - p)}{p_0} = \text{a constant} \quad . \quad . \quad . \quad . \quad (1)$$

and this expression is independent of the temperature at which measurements are made even though the numerical value of p_0 increases rapidly with rising temperature. This ratio (1), is termed the "relative lowering of the vapour pressure."

A little later, Wüllner (1860), also working with aqueous solutions of salts confirmed the experimental results of von Babo and in addition suggested that the lowering of vapour pressure is proportional to the concentration of the solution. Raoult (1887) also confirmed the findings of von Babo, and arising from measurements made with a number of solutes, in organic solvents in particular, proposed the following relationship—

$$\frac{p_0 - p}{p_0} = \frac{n_2}{n_1 + n_2} = x_2 \quad . \quad . \quad . \quad . \quad (2)$$

where n_1 = number of mols of solvent, n_2 = number of mols of solute, and x_2 = mol fraction of solute.

TABLE 24

Solubility Characteristics of some Common Compounds

Mainly Soluble Substances

Compound	Exceptions
Nitrates	
Acetates	
Chlorides, bromides and iodides	Silver, mercury (Hg^+) and lead, $PbCl_2$ and $PbBr_2$ are sparingly soluble in cold water (1g per 100 ml at 20°C) but more soluble in hot water (3g and 5 g respectively per 100 ml at 100°C)
Sulphates	$BaSO_4$, $SrSO_4$, $PbSO_4$. The following are sparingly soluble, $CaSO_4$, Ag_2SO_4, Hg_2SO_4
All salts of sodium, potassium and ammonium	$NaSb(OH)_6$, $K_3Co(NO_2)_6$, K_2PtCl_6, $(NH_4)_2PtCl_6$, $(NH_4)_3Co(NO_2)_6$

Mainly Insoluble Substances

Compound	Exceptions
Hydroxides	Hydroxides of the alkali metals, NH_4OH and $Ba(OH)_2$. The following are sparingly soluble, $Ca(OH)_2$ and $Sr(OH)_2$
Carbonates	Carbonates of the alkali metals and ammonium— *Note*: Many hydrogen carbonates, [e.g. $Ca(HCO_3)_2$] are soluble
Phosphates	Phosphates of the alkali metals and ammonium *Note*: Many hydrogen phosphates [e.g. $Ca(H_2PO_4)_2$] are soluble
Sulphides	Sulphides of the alkali metals, ammonium and the alkaline earth metals

By subtracting unity from both sides of (2) it will be clear that, if x_1 = mol fraction of the solvent—

$$\frac{p}{p_0} = 1 - x_2 \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

And since, $(x_1 + x_2) = 1$

therefore, $$\frac{p}{p_0} = x_1$$

and $$p = p_0 x_1 \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

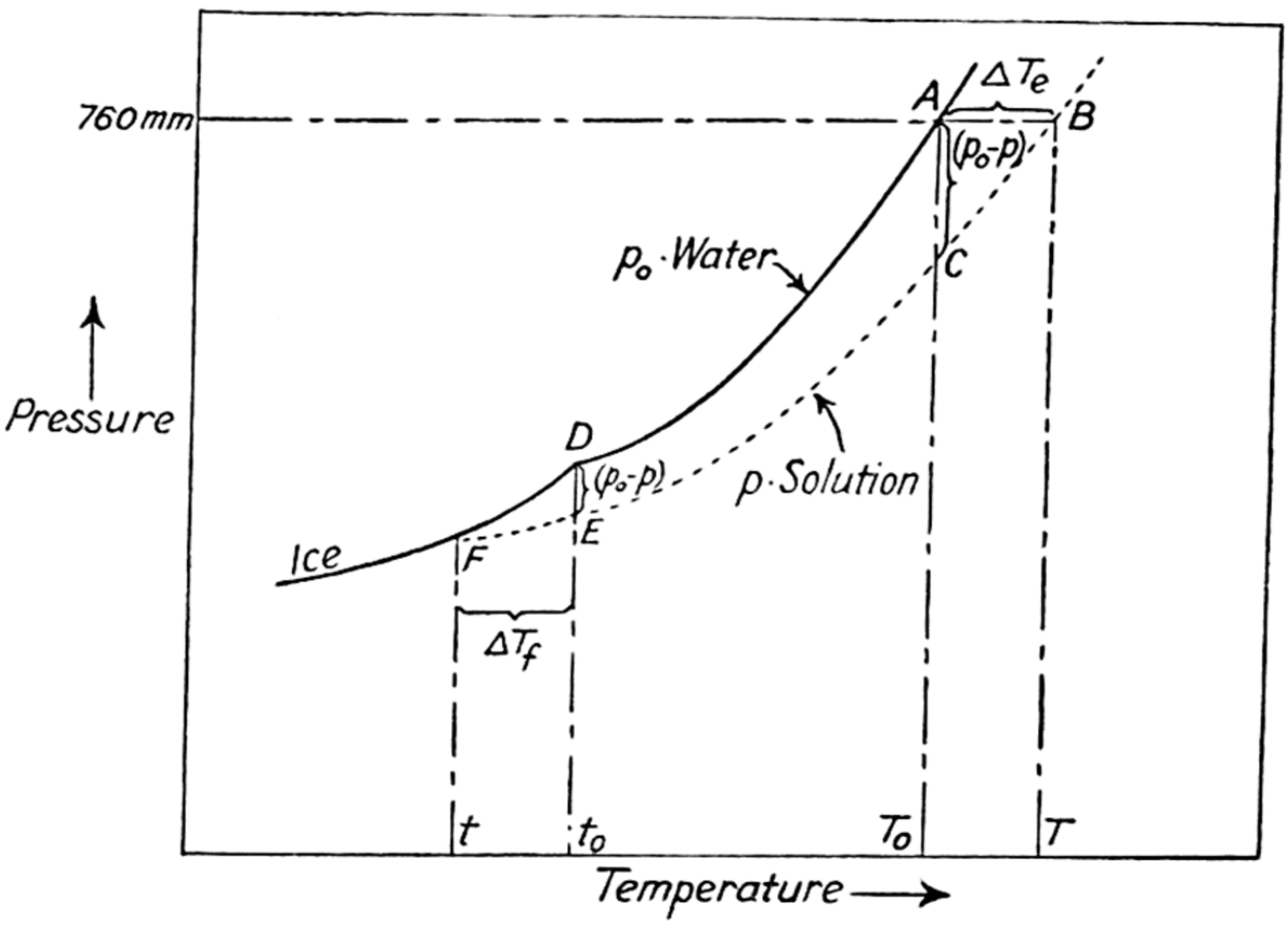


FIG. 49. Variation with Temperature of Vapour Pressure of Pure Water and of an Aqueous Salt Solution

Thus, the vapour pressure of the solvent in a solution obeying Raoult's equation (2) is directly proportional to the mol fraction of the solvent. Equations (2) and (2b) may therefore be regarded as alternative methods of expressing what is known as Raoult's Law. The variation of vapour pressure with temperature for pure water and for an aqueous salt solution are shown graphically in Fig. 49 from which it will be noted that the value of $(p_0 - p)$ increases with rising temperature and also, therefore, with increasing pressure.

Determination of Molecular Weights. Using equation (2), measurements of the lowering of vapour pressure may be employed to determine the molecular weights of substances in solution.

If w_2 g of solute of molecular weight M_2 are dissolved in w_1 g of solvent of molecular weight M_1, then the number of mols of solute and solvent

are $n_2 = w_2/M_2$, and $n_1 = w_1/M_1$ respectively, and substituting in Raoult's equation (2)

$$\frac{p_0 - p}{p_0} = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2} \quad . \quad . \quad . \quad (3)$$

In dilute solutions the numerical value of n_2 is small in comparison with n_1, and thus may be neglected, so that (3) may be simplified thus—

$$\frac{p_0 - p}{p_0} = \frac{w_2 M_1}{M_2 w_1} \quad . \quad . \quad . \quad . \quad (4)$$

Thus, by measuring the vapour pressure of the pure solvent, p_0, and that of the solution, p, containing known weights of solvent and solute, w_1 and w_2 respectively, and knowing the molecular weight of the solvent, M_1, it is possible to evaluate the molecular weight of the solute, M_2.

Methods for Measuring Vapour Pressure

A number of different methods are employed for the measurement of the vapour pressure of solutions.

Differential Methods. Although the use of a barometer is capable of application in certain cases, it is usually not sufficiently precise to be generally useful in this connexion. With the object of overcoming these difficulties various manometric methods have been suggested.

In a method introduced by Menzies, the solution is made to serve as its own manometric liquid. The lowering of vapour pressure is measured at the boiling point so the value of $(p_0 - p)$ is much greater than at room temperature. The apparatus is shown in Fig. 50. The bulb *A* contains air-free solvent, which is also placed in the inner graduated tube *B*. Heat is applied to the bulb *A* and by closing the tap *E* connecting the apparatus to a condenser, and raising the stopper *D*, vapour is forced through the tube *C* into the liquid contained within tube *B* so raising it to the boiling point. The tap *E* is then slowly closed and the stopper *D* lowered into position. As bulb *A* and tube *B* both contain boiling solvent, the levels in *B* and *C* should be the same; in actual fact the level in *C* is slightly higher owing to the capillary effect and this difference is read off on the graduations on tube *C*. Heating is stopped, a weighed

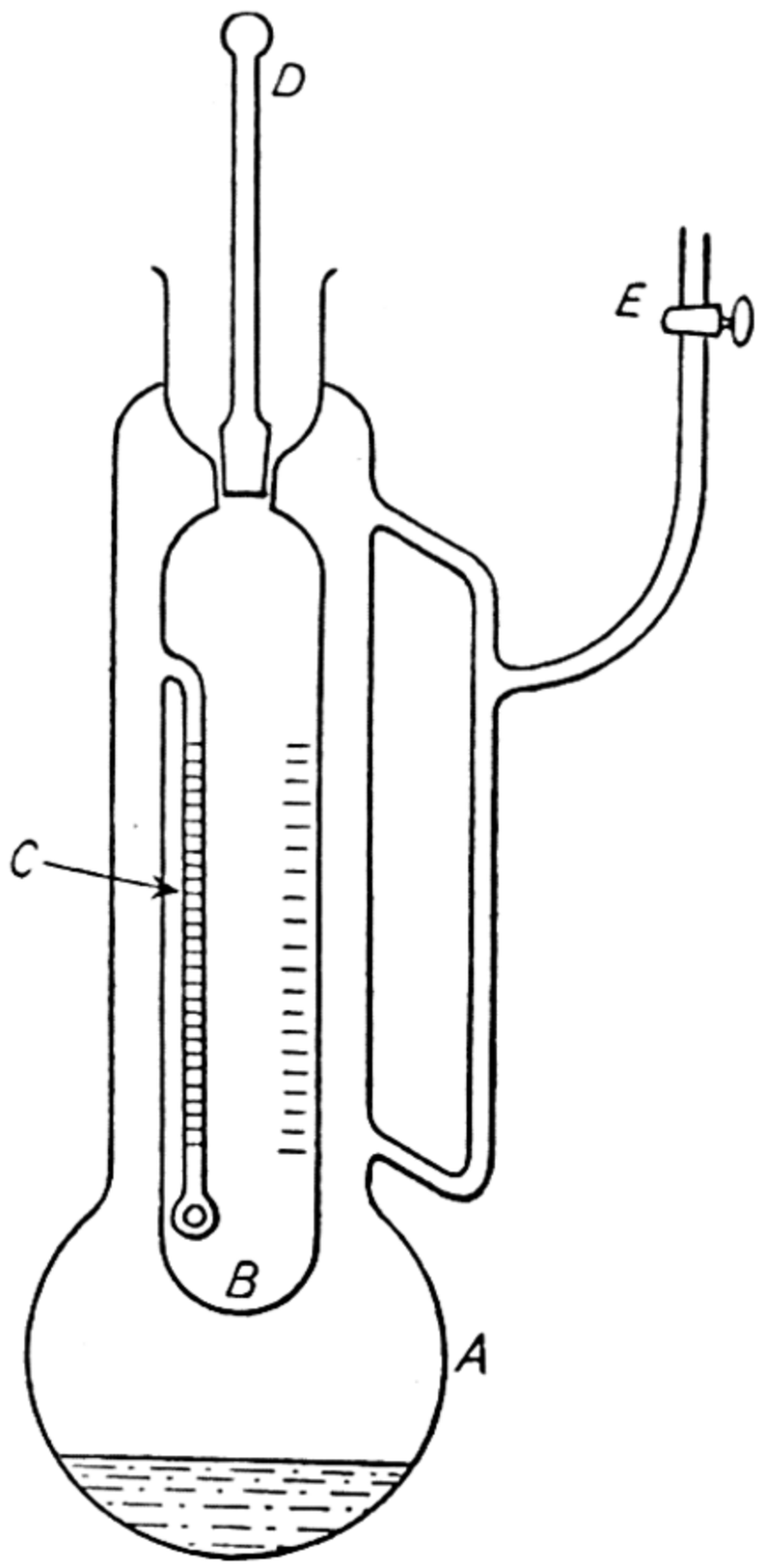


FIG. 50. Menzies Apparatus for the Measurement of Lowering of Vapour Pressure

amount of solute added via the ground neck to the tube *B*, and the "blowing through" procedure, as described above, repeated. The pressure of the vapour in bulb *A* containing pure solvent is now greater than that in tube *B* containing the solution, so that the level of the liquid in tube *C* will be depressed below that of the surrounding solution. This difference of level, after making allowance for capillarity, gives $(p_0 - p)$ in millimetres of the solution at its boiling point and this value may then be converted into millimetres of mercury. The value of p_0 is, of course, the vapour pressure at its boiling point, and thus is equal to the barometric pressure. The weight of the solute is known, and the weight of the solvent may be calculated from the volume of the solution in tube *B* as read off from the graduations on the side of this tube.

Transpiration Method. The transpiration method as outlined on p. 105 may be employed for the measurement of the lowering of vapour pressure. In this method dry air is drawn in succession through a series of Liebig bulbs (*see* Fig. 51), containing respectively the solution, the pure solvent (water), and an absorbent such as sulphuric acid.

(Arrows indicate direction of flow of air)

Set *A*	→	Set *B*	→	Set *C*
Solution with vapour pressure $= p$		Pure solvent with vapour pressure $= p_0$		Concentrated sulphuric acid
(In this set the air is saturated with water vapour up to p)		(In this set the air is saturated with water vapour up to p_0)		(In this set the water vapour is completely absorbed)

FIG. 51. Layout of Apparatus used to Determine Vapour Pressure by the Transpiration Method

In passing through the first set of bulbs (Set *A*, Fig. 51), the initially dried air is saturated with water vapour at pressure p, and this set of bulbs decreases in weight by an amount proportional to p; on entering the second set of bulbs (Set *B*) containing the pure solvent the pressure of the vapour is increased to p_0 and the second set of bulbs suffers a decrease in weight proportional to $(p_0 - p)$. On passing through the third set of bulbs (Set *C*), all the water is absorbed and the water vapour pressure is reduced from p_0 to zero, and so the gain in weight of this third set of absorption bulbs is proportional to p_0. The ratio of the loss in weight of the second set of bulbs to the gain in weight of the third set is thus equal to $(p_0 - p)/p_0$, the relative lowering of vapour pressure.

$$\frac{\text{Loss in weight of Set } B}{\text{Gain in weight of Set } C} = \frac{\text{Lowering of vapour pressure}}{\text{Vapour pressure of pure solvent}}$$

$$= \frac{p_0 - p}{p_0}$$

Dew-point Method. Should a vapour at any given pressure be chilled, the liquid phase commences to form at the temperature for which that pressure is the saturation value. This principle is employed in the so-called "Dew-point" method for determining vapour pressure. One form of

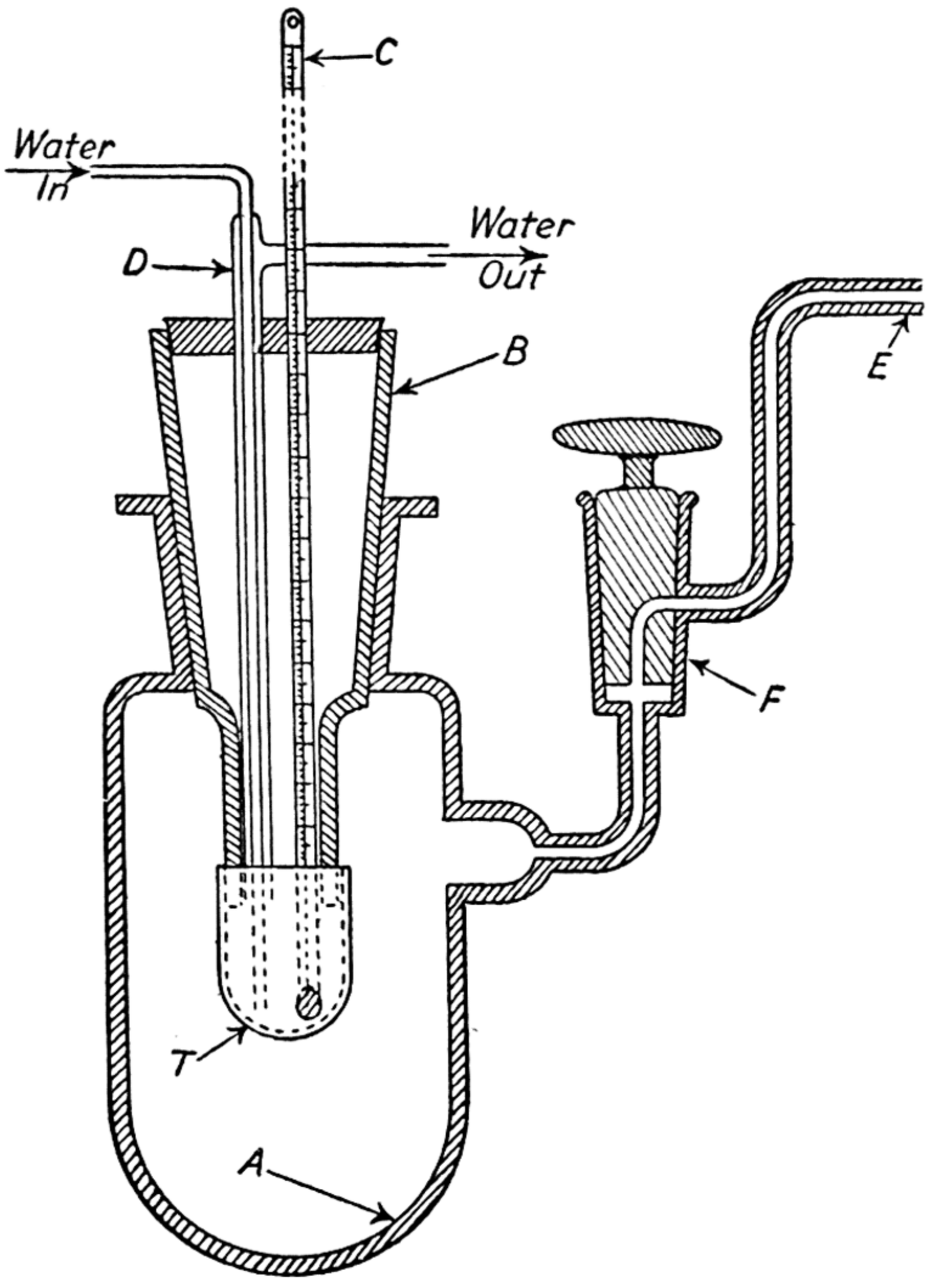


FIG. 52. Dew-point Apparatus for the Measurement of Lowering of Dew Point

apparatus is shown in Fig. 52. The aqueous solution under examination is placed in the bulb *A*, the bulb is evacuated through tube *E*, and the tap *F* then closed. The whole apparatus is then placed in a thermostat. Water is allowed to circulate through tube *B* via the inlet tube *D*. Sealed on to the end of the tube *B* is a silver thimble, *T*. The temperature of the circulating water is varied and as its temperature is progressively lowered a temperature is ultimately reached at which dew forms on the outside of the silver thimble; the temperature at which such dew forms is then read off on the thermometer, *C*.

The saturation vapour pressure of water at this temperature is read off from tables and this is the vapour pressure of water vapour in the bulb *A* at the temperature of the thermostat. The molecular weight of the solute may then be calculated as in the previous methods.

Elevation of the Boiling Point

The boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure. Since the addition of a non-volatile solute to a pure solvent lowers the vapour pressure of the latter, it follows directly that the boiling point of the solution must be higher than that of the pure solvent. This is made clear by Fig. 49 (p. 138), from which it will be evident that the vapour pressure of a solution is always less than that of a pure solvent measured at the same temperature. If the boiling point of the pure solvent is T_0 (Fig. 49) and that of the solution, T, then the elevation of the boiling point is $(T - T_0) = \Delta T_e$, which is represented by the line AB. At the temperature T_0 the lowering of vapour pressure $(p_0 - p)$ is represented by the line AC. Since at temperature T_0 the vapour pressure of the pure solvent p_0 is of a constant value—that is, the atmospheric pressure—then at this temperature AC is proportional to $(p_0 - p)/p_0$. Further, since in the region of the boiling point the two vapour pressure curves approximate very closely to parallel lines then the ratio AB/AC will be of a constant value. In other words, the elevation of the boiling point is proportional to the relative lowering of the vapour pressure.

According to equation (2),

$$\frac{(p_0 - p)}{p_0} = x_2$$

and if

$$\Delta T_e = \frac{(p_0 - p)}{p_0}$$

then,

$$\Delta T_e = k_e x_2 \quad . \quad . \quad . \quad . \quad (4)$$

where k_e = a constant.

For dilute solutions the approximate form of (2) may be employed, viz.—

$$\frac{(p_0 - p)}{p_0} = \frac{w_2 M_1}{M_2 w_1} \quad . \quad . \quad . \quad . \quad (5)$$

therefore,

$$\Delta T_e = \frac{k_e w_2 M_1}{M_2 w_1} \quad . \quad . \quad . \quad . \quad (6)$$

which may be rewritten,

$$M_2 = \frac{k_e w_2 M_1}{\Delta T_e w_1} \quad . \quad . \quad . \quad . \quad (7)$$

where k_e = a constant which is specific for each solvent, w_1 = weight of

solvent, w_2 = weight of solute, M_1 = molecular weight of solvent and M_2 = molecular weight of solute.

This expression may then be employed for the determination of the molecular weight of a solute from measurements of boiling point elevation obtained with known weights of solvent and solute. The numerical value of k_e may be determined for the gramme molecular weight, or any other weight of solvent. In Table 25 are given values for this constant for 1000 g of solvent of various solvents. For this weight of solvent this constant is termed the *molecular elevation constant* or the *ebullioscopic constant*.

TABLE 25

Values of Ebullioscopic Constants

Solvent	B.P. °C	Ebullioscopic Constant (K_e)	
		For 1000 g of Solvent	For 1000 ml of Solvent
Acetone . . .	56·5	1·73	2·23
Benzene . . .	80·2	2·60	3·27
Carbon disulphide .	46·2	2·35	2·60
Chloroform . . .	61·0	3·85	2·60
Ethyl alcohol . .	78·3	1·19	1·58
Di-ethyl ether . .	35·4	2·16	3·03
Water	100·0	0·52	0·54

Equation (7) may now be rewritten as follows—

$$M_2 = \frac{K_e 1000 w_2}{\Delta T_e w_1} \quad . \quad . \quad . \quad . \quad (8)$$

where K_e = ebullioscopic constant for 1000 g of solvent.

Van't Hoff (1886) has shown that the ebullioscopic constant may be determined by calculation from thermo-dynamical data and—

$$K_e = \frac{RT_0^2}{1000 l_e} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where R = gas constant, T = boiling point of solvent (on Absolute scale), and l_e = latent heat of vaporization per gramme of solvent.

If the volume but not the weight of the solvent is known the appropriate constant may be calculated from the expression—

$$K_e' = \frac{K_e}{\text{Density}} \quad . \quad . \quad . \quad . \quad (10)$$

where K_e = ebullioscopic constant for 1000 g of solvent and K_e' = ebullioscopic constant for 1000 ml of solvent.

Experimental Determination of Boiling Point Elevation

Beckmann's Method. In this method, which is now largely of historical interest only, a weighed amount of solvent (approximately 20 g) is introduced into tube *A* (Fig. 53) which has a thick platinum wire *P* sealed in the bottom to facilitate the conduction of heat to the solution. The boiling point of the solvent is then determined by means of the accurate thermometer *T*. The tube *A* is connected to a condenser to minimize loss of liquid. A weighed pellet of the solute is then introduced via neck *B* and the boiling point of the solution determined.

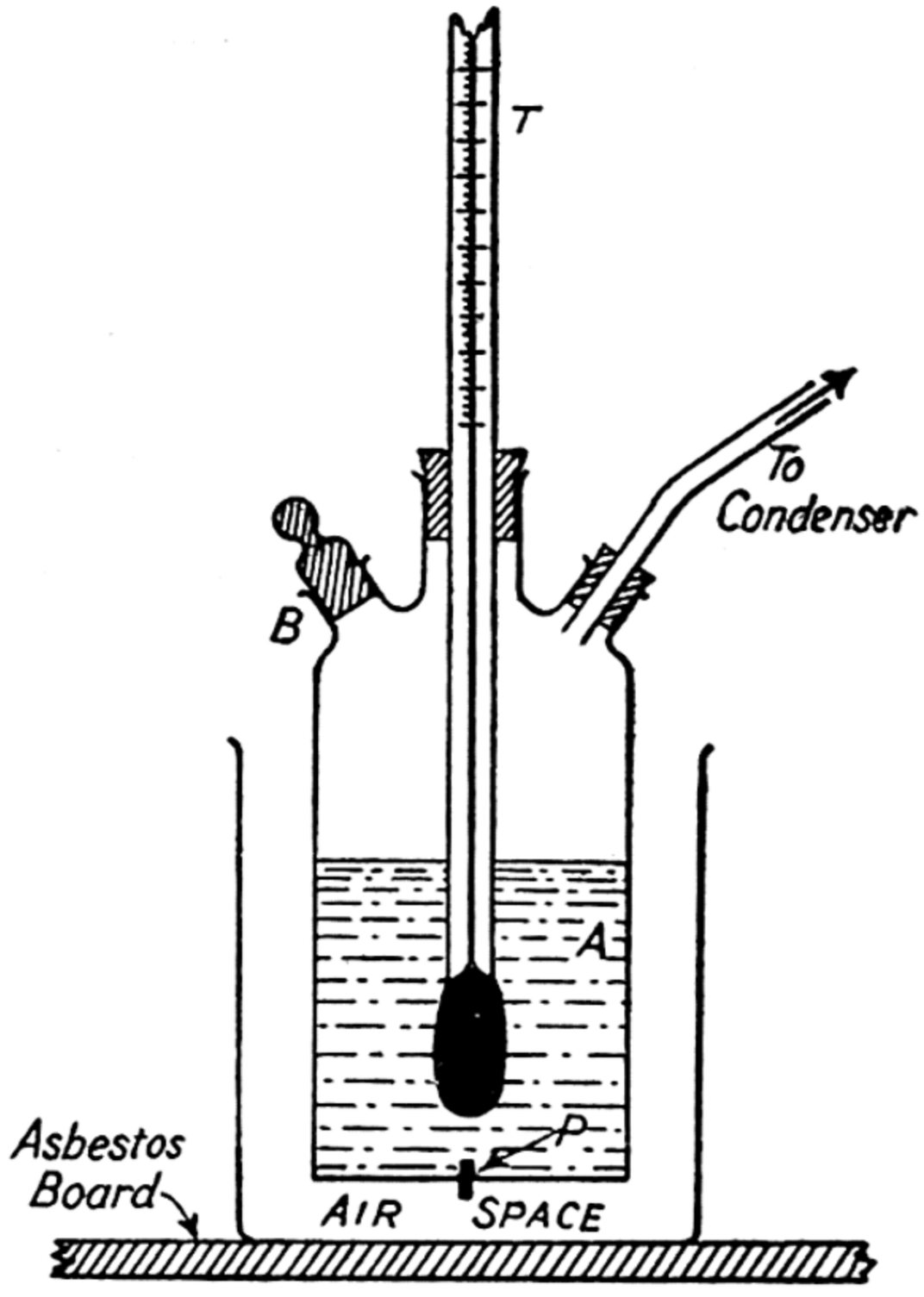


FIG. 53. Beckmann's Apparatus for Measurement of the Elevation of Boiling Point

Having obtained from tables the numerical value of the ebullioscopic constant the molecular weight of the solute may then be calculated by the use of equation (8).

Landsberger's Method. The apparatus used in this method is shown in Fig. 54. In this apparatus a small volume of solvent is placed initially in the graduated tube *B* contained within the jacket *A*, and solvent vapour is passed from the distillation flask *D*, via the delivery tube *E*, into graduated tube *B*, where it ultimately condenses and raises the temperature of the

solvent in this tube to its boiling point. Excess solvent vapour in the tube *B*, escapes through the orifice *O* and is condensed by the condenser C.

A weighed amount of solute is then added to the tube *B*, and the temperature of the solution raised as described above. When constancy of temperature is attained it is read off and the volume of the solution, as indicated by the graduations on tube *B*, at once recorded.

It is important to note here that the solution is raised to its boiling point by condensation of solvent vapour entering tube *B*, and because of the liberation of the latent heat of vaporization, the temperature of the

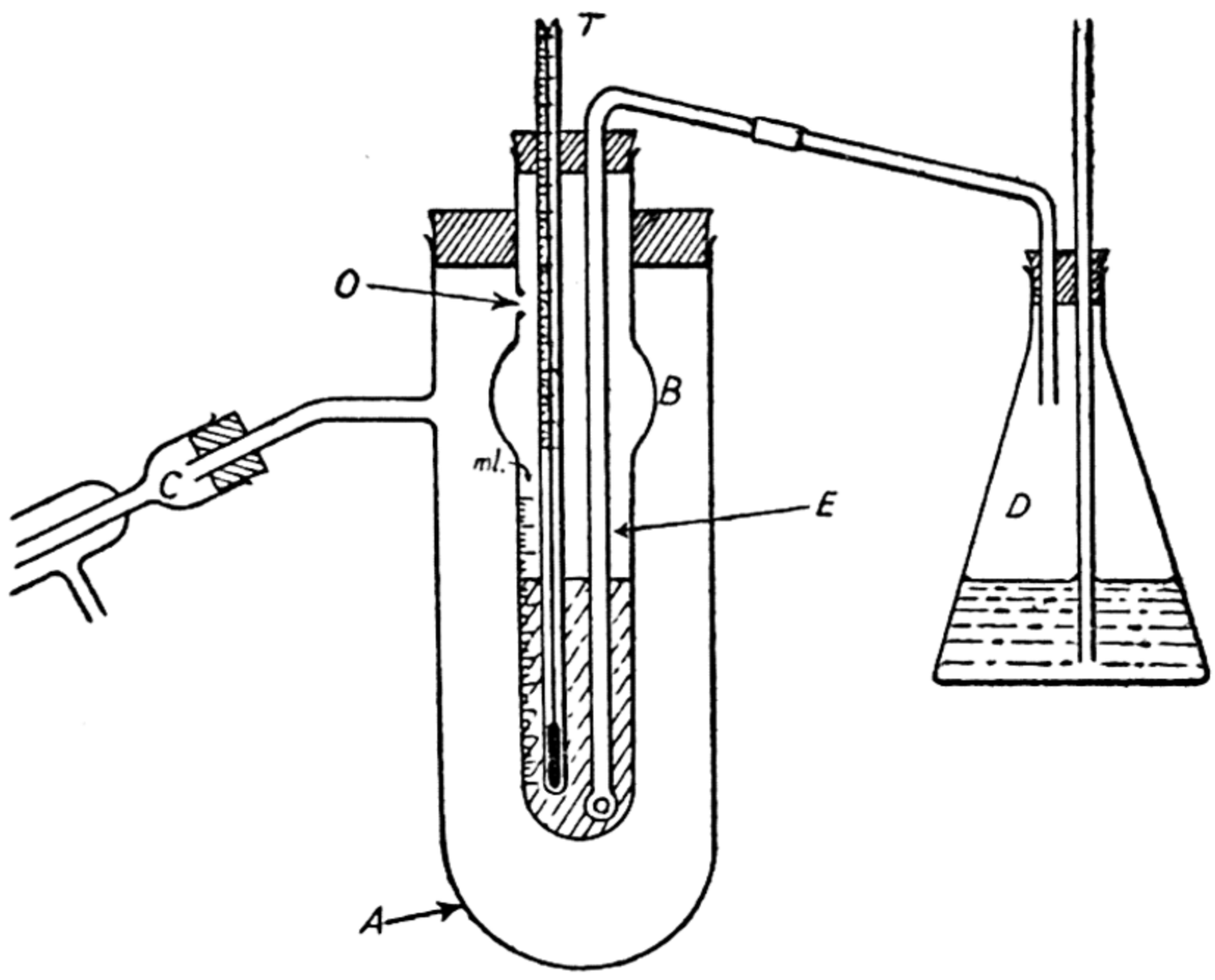


FIG. 54. Landsberger's Apparatus for Measurement of Elevation of Boiling Point

solution is finally raised to its boiling point. The thermometer employed should be graduated in tenths of a degree and be capable of being read to 0·01°C.

With the experimental data obtained, and by employing equation (8) the molecular weight of the solute may then be calculated.

Cottrell's Method. It has been shown that the boiling points of most common solvents are approximately 0·1°C high at a depth of 3 to 4 in. below the liquid surface on account of the hydrostatic pressure of the column of liquid. The result is that the thermometer indicates the mean boiling point which varies throughout the depth of the liquid. These difficulties have been overcome by Cottrell who has devised a method in which the thermometer is placed in the vapour *above* the liquid surface, the boiling solution being caused to pump itself continuously over the thermometer bulb.

One form of Cottrell's apparatus is shown in Fig. 55. Tube *A* contains the boiling solvent or solution as the case may be, a thick platinum wire *B* sealed in the bottom of tube *A* facilitating uniform boiling. The side tube *C* leads to a condenser and the sheath *D* prevents the chilled condensate from coming into contact with the thermometer *T*.

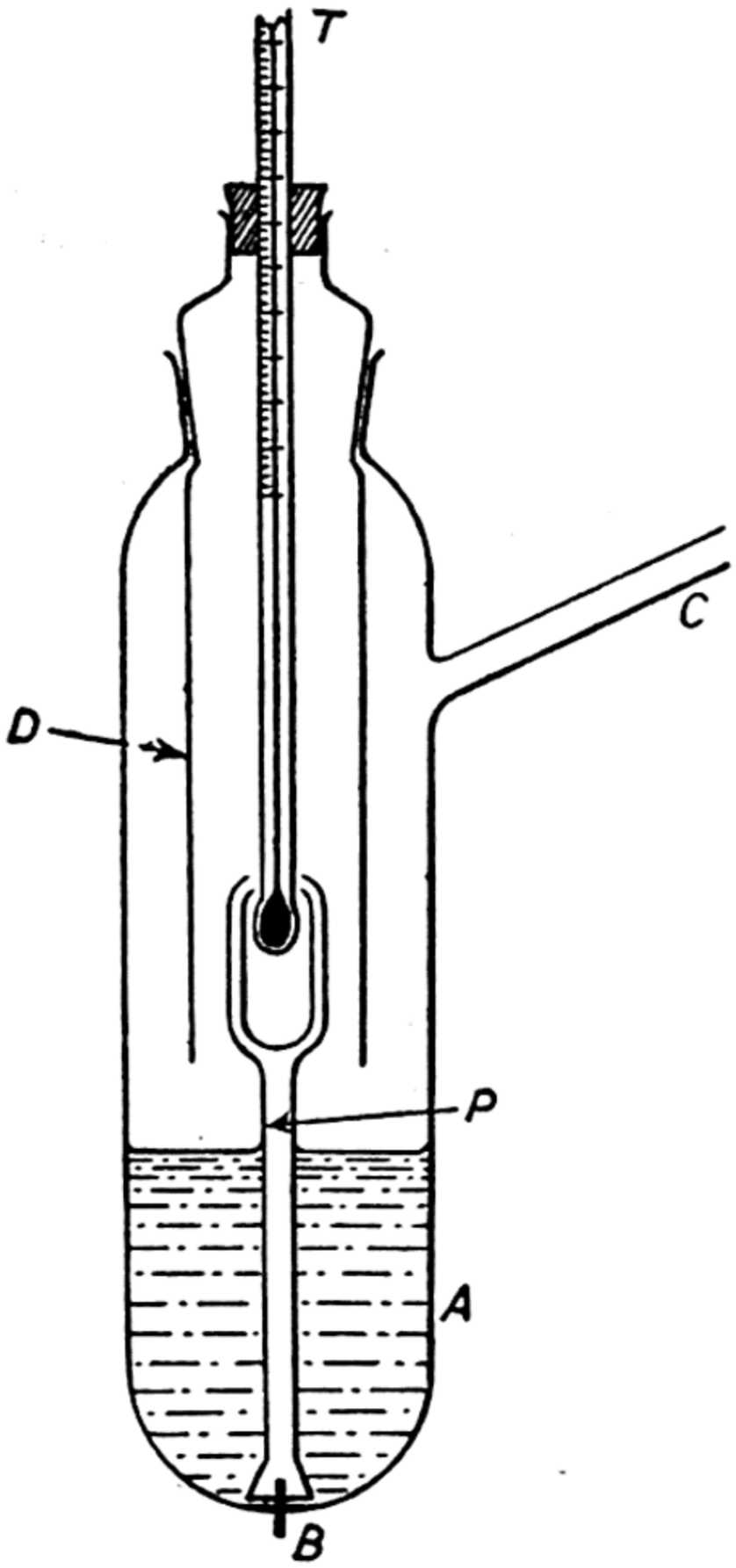


FIG. 55. Cottrell's Apparatus for Measurement of Elevation of Boiling Point

When the tube *A* is heated by means of a small flame, the liquid boils and passes upwards through the pump *P* from the end of which it pours over the thermometer bulb. The addition of a known weight of solute and the reading off of the volume of solution after a constant boiling point has been attained are carried out as in the Landsberger method.

Depression of the Freezing Point

A further result following from the lowering of the vapour pressure of a solution by a non-volatile solute is that the freezing point of the solution is lower than that of the pure solvent. This fact has been known for many years and Blagden (1788) was one of the first to observe that *the depression of the freezing point was proportional to the concentration of the solution;* this generalization is usually known as Blagden's Law. Resulting from experiments using both aqueous solutions of acids, bases and salts, as well as non-aqueous solutions of organic compounds, Raoult (1878–86) found that equimolecular solutions of different substances of a similar type in a given solvent exhibited the same freezing point.

A little later Beckmann (1888) introduced improvements in the experimental technique involved in *cryoscopy*—that is, the study of the freezing points of solutions—with the result that it was possible to carry out such determinations with the utmost precision.

The relationship between vapour pressure and the freezing points of a solvent and a solution is depicted graphically in Fig. 49. The freezing point of the solvent (water), t_0, is indicated by *D*, the point of intersection of the vapour pressure curves for ice and water respectively since at this temperature the solid and liquid phases exist together in equilibrium. In a similar manner the freezing point of the solution is indicated by the point *F* at the

temperature t since at this temperature the solution and the pure solid solvent (ice) are in equilibrium. Thus, the lowering of the freezing point is $(t_0 - t) = \Delta T_f$. Now the line DE (Fig. 49) is equivalent to the lowering of the vapour pressure $(p_0 - p)$ at the temperature t_0, and since at t_0 the numerical value of p_0 is constant, it follows, as shown previously when discussing the theoretical principles underlying the elevation of the boiling point (page 142), that DE is proportional to the relative lowering of the vapour pressure. Since, in the vicinity of the freezing point the vapour pressure curves may be regarded as parallel the ratio FE/DE is of a constant value. Thus, the depression of the freezing point is proportional to the relative lowering of the vapour pressure, and hence to the mol fraction of the solute, x_2.

Therefore, as in the case of equation (6)

$$\Delta T_f = \frac{k_f w_2 M_1}{M_2 w_1} \quad . \quad . \quad . \quad . \quad (11)$$

which may be rewritten as follows—

$$M_2 = \frac{k_f w_2 M_1}{\Delta T_f w_1} \quad . \quad . \quad . \quad . \quad (12)$$

where w_1 = weight of solvent, w_2 = weight of solute, M_1 = molecular weight of solvent, M_2 = molecular weight of solute, ΔT_f = depression of the freezing point, and k_f = a constant.

The molecular weight of the solute may be evaluated by the use of equation (12). Comparison should be made with equation (8) employed for the determination of the molecular weight of the solute from ebullioscopic data. For the determination of the molecular weight equation (12) is more conveniently written in the following form—

$$M_2 = \frac{K_f 1000 w_2 M_1}{\Delta T_f w_1} \quad . \quad . \quad . \quad . \quad (13)$$

where K_f = the cryoscopic constant for 1000 g of solvent. Other symbols have their previous significance.

The cryoscopic constant may be calculated from thermodynamic data by the use of the following expression (cf. equation (9))

$$K_f = \frac{R t_0^2}{1000 l_f} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where R = gas constant, t_0 = freezing point of solvent on Absolute temperature scale and l_f = latent heat of fusion per gramme of solvent.

Some typical values for the cryoscopic constants for a number of common solvents are given in Table 26.

TABLE 26

Values of Cryoscopic Constants

Solvent	F.P. (°C)	Cryoscopic Constant per 1000 g of Solvent (K_f)
Acetic acid . . .	17·0	3·90
Benzene . . .	5·4	5·10
Bromoform . . .	7·6	14·3
Camphor . . .	175·0	40·0
Cyclohexane . . .	6·4	20·2
Naphthalene . . .	80·0	7·0
Nitrobenzene . .	3·6	6·9
Phenol	39·0	5·3
Water	0·0	1·86

Experimental Determination of Freezing Point Depression

Freezing point measurements may be made with great precision and are frequently employed therefore for the determination of molecular weights.

In making such determinations however two facts must be kept constantly in mind; they are—

(*a*) Dilute solutions should be employed, and

(*b*) It is essential that the crystals which separate on chilling consist entirely of the pure solvent.

If concentrated solution and/or solid solutions form on chilling, the mathematical expressions for the molecular weight determination are invalid.

Beckmann's Method. The apparatus used in this method is depicted diagrammatically in Fig. 56.

A known weight (e.g. 20 g) of solvent is placed in the freezing-point tube *A* which is fitted with a stirrer *D* and a very sensitive thermometer *T*. This tube is fitted inside another tube *B*, so leaving an air space between the two tubes. This assembly is then immersed in a vessel *C* which contains a suitable freezing mixture (in which a stirrer *F* is immersed), whose temperature is not more than 5°C below the freezing point of the pure solvent contained in tube *A*. The pure solvent is thus chilled and its temperature is allowed to fall until it is about 0·5°C below its freezing point when the solvent is stirred vigorously. Crystallization commences at once and the temperature of the solvent rises to its freezing point which is then recorded. To the solvent a weighed amount of solute is then added via the side tube *E* and the freezing point of the solution determined in the

manner described above. This procedure is then repeated with several successive additions of solute.

The thermometer usually employed in this method is of the type originally devised by Beckmann, being usually referred to as the "Beckmann thermometer." In essence, the Beckmann thermometer consists of a very

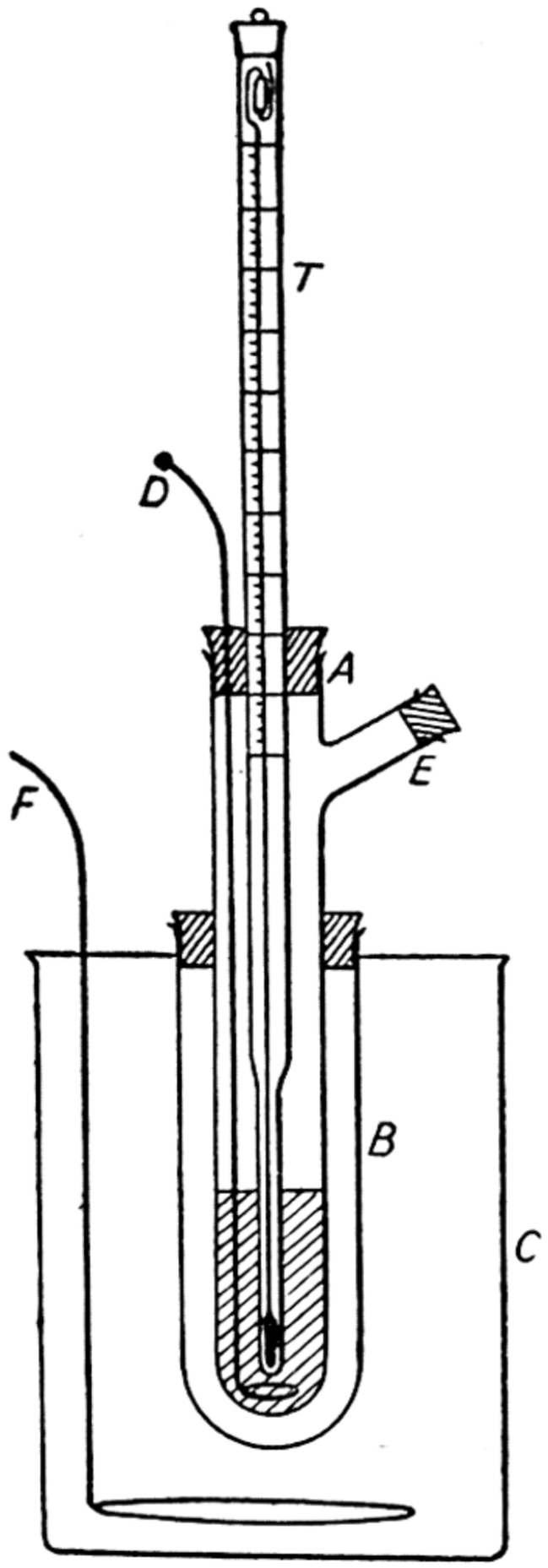


FIG. 56. Beckmann's Apparatus for Determination of Molecular Weights from Freezing Point Determinations

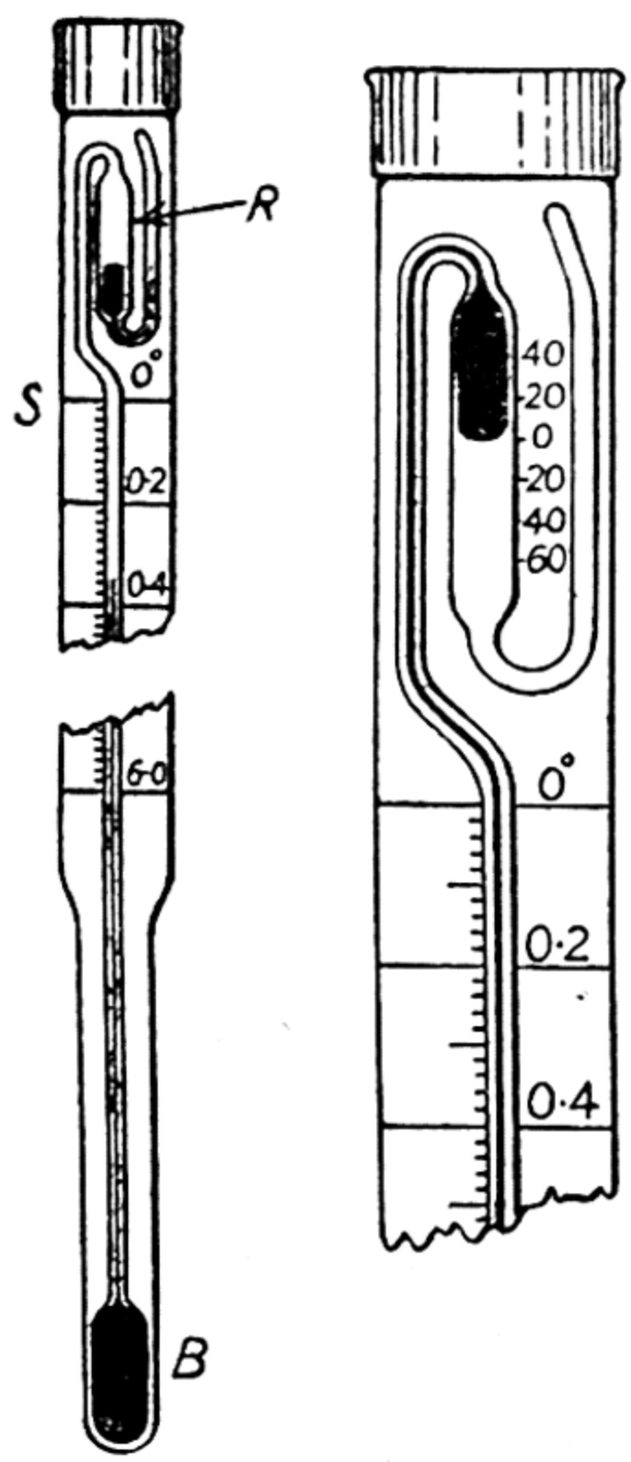


FIG. 57. Constructional Details of Beckmann Thermometer

sensitive thermometer which may have mercury transferred to or from the bulb *B* (Fig. 57). Thus the thermometer may be employed over a wide range of temperature and for a variety of solvents whilst retaining a high degree of accuracy on account of the fine capillary. In operation, use is made of the reservoir *R*; for example, if it is desired to withdraw mercury from the reservoir when employing solvents having low freezing points the thermometer is inverted and the upper end tapped gently so as to bring the mercury in *R* into connexion with the capillary. The bulb *B* is

then very cautiously warmed so that the mercury in the capillary rises, and ultimately unites with the mercury in the reservoir. Bulb *B* is then cooled in a water bath whose temperature has been adjusted to lie 2 to 3°C above the freezing point of the pure solvent to be employed in the molecular weight determination. After allowing sufficient time for the mercury in bulb *B* to attain the temperature of the water bath the top of the thread is tapped, thus causing the mercury in the reservoir to separate from the capillary. This setting of the thermometer is then tested by immersing the thermometer bulb in the freezing solvent when the mercury in the capillary should stand just below the uppermost graduation on the scale *S*.

Rast's Method. From Table 26 it will have been noted that the cryoscopic constant for camphor is unusually high, that is, 40. This fact is of considerable importance in that it is thus possible to make determinations of molecular weight when only very small amounts of the solute soluble in camphor are available. A few milligrammes of the solute are mixed with about ten times their weight of camphor and the mixture melted. After solidification has occurred the mixture is finely ground and a known weight transferred to a moderately wide melting-point tube attached to a thermometer bulb. On account of the large cryoscopic constant for camphor a thermometer graduated in tenths of degrees permits of readings of sufficient accuracy being obtained. The thermometer with the attached tube is heated in a paraffin bath and the temperature at which the last traces of solid camphor melt is taken as the freezing point of the solution.

OSMOSIS AND OSMOTIC PRESSURE

If the two compartments of a divided cell, in which a piece of animal membrane (e.g. pig's bladder) constitutes the common partition wall, are filled with water and alcohol respectively it will be found that the water will pass through the membrane into the alcohol but that the alcohol is unable to pass through the membrane into the water. This fact was first noted by the Abbé Nollet (1748). In a similar way if red blood corpuscles are placed in distilled water they swell and finally burst, since the cell walls are permeable to water but not to certain of the substances in solution within the cell, and water passes inwards into the cell in an effort to establish a condition of equilibrium (i.e. equality of water vapour pressure) between the water outside the cell and the solution within the cell. In this particular case, equilibrium is not attained since the cell wall lacks the strength to withstand the hydrostatic pressure which would obtain when the water vapour pressure of the solution inside the cell equalled the vapour pressure of the distilled water in which the cell is immersed.

Van't Hoff (1886) suggested that such materials as pig's bladder and the cell walls of red blood corpuscles, which permit the diffusion of pure solvent but not that of the solution, should be termed *semipermeable membranes*.

This phenomenon of the spontaneous flow of a solvent (often water) through a suitable membrane into a solution, or from a dilute to a more concentrated solution is known as *osmosis*. The phenomenon of osmosis may also be demonstrated by covering the large open end of a thistle funnel with a piece of pig's bladder (or alternatively with parchment paper or a piece of "Cellophane"), the funnel is then inverted and filled with a concentrated sugar solution and allowed to dip into a beaker containing distilled water (*see* Fig. 58). The water level in the stem of the thistle funnel will rise until the hydrostatic pressure due to the head of water causes water to flow from the thistle funnel, through the membrane, into the beaker at exactly the same rate as water is caused, by osmosis, to flow into the thistle funnel from the beaker.

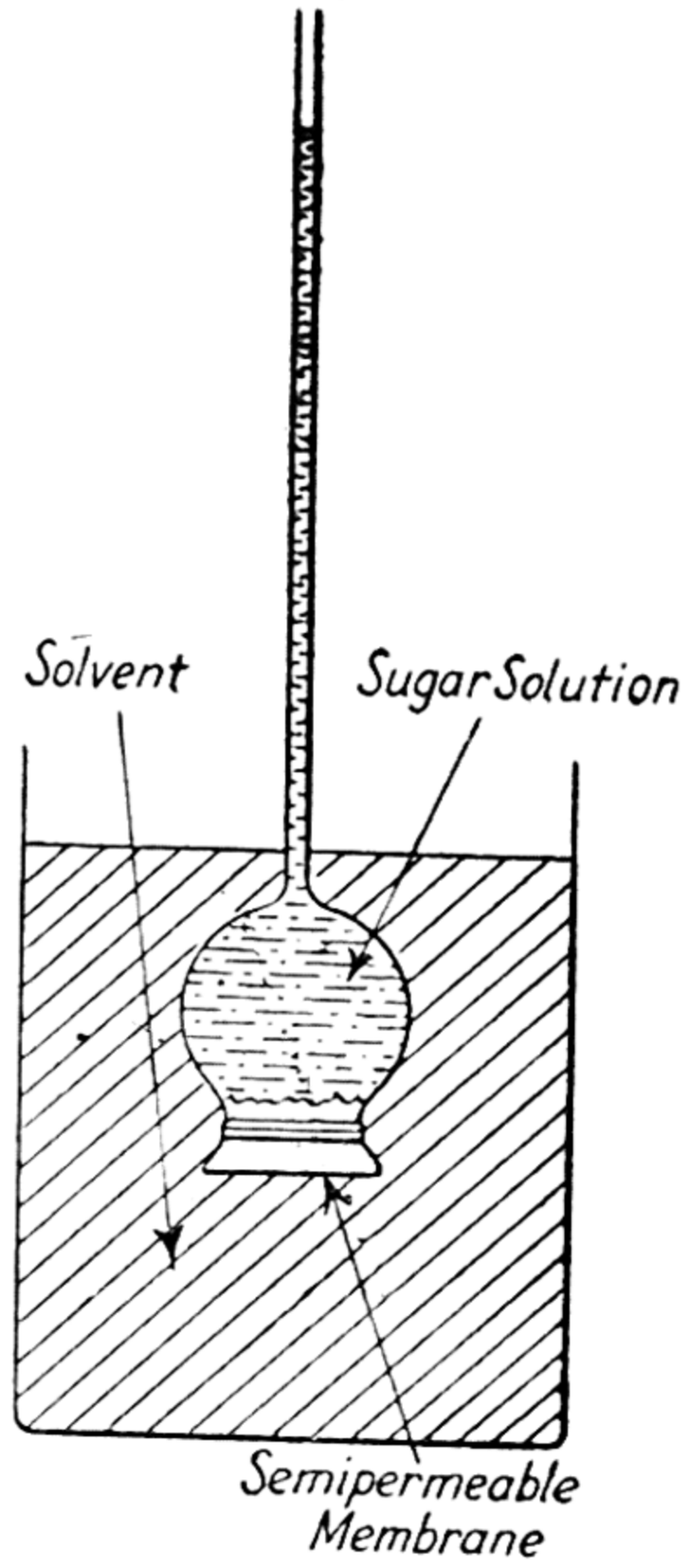


FIG. 58. Experiment to Demonstrate Osmosis

Such membranes as those described above are not very satisfactory inasmuch as they are not completely semipermeable and the solute tends to leak out of the retaining vessel into the pure solvent. In addition, such arrangements suffer from the disadvantage that the solution contained within the thistle funnel is diluted considerably by the water which passes inwards.

After examining a large number of substances, Traube (1864) found that copper ferrocyanide, $Cu_2[Fe(CN)_2]$ was capable of acting as an efficient membrane, being much superior to animal and vegetable membranes in this respect. Copper ferrocyanide is obviously far too fragile a substance to use as a semipermeable membrane when in the unsupported condition, but Pfeffer (1877) showed that by precipitating this compound within the pores of an unglazed porous pot it is possible to strengthen the membrane enormously, and if, in addition, a closed manometer be employed it is possible to make measurements of the pressure due to osmosis without the solvent actually entering, and therefore diluting, the solution under investigation. This pressure due to osmosis is termed the *osmotic pressure of a solution*.

It is important to appreciate at this point that if a progressively increasing pressure is exerted from an external source on the solution, the flow of solvent into the solution through the semipermeable membrane will slacken, then cease and finally solvent will flow from the solution into the solvent. Thus, the osmotic pressure of a solution may be defined as the

pressure which must be exerted upon a solution so as just to prevent the flow into it of solvent through a semipermeable membrane.

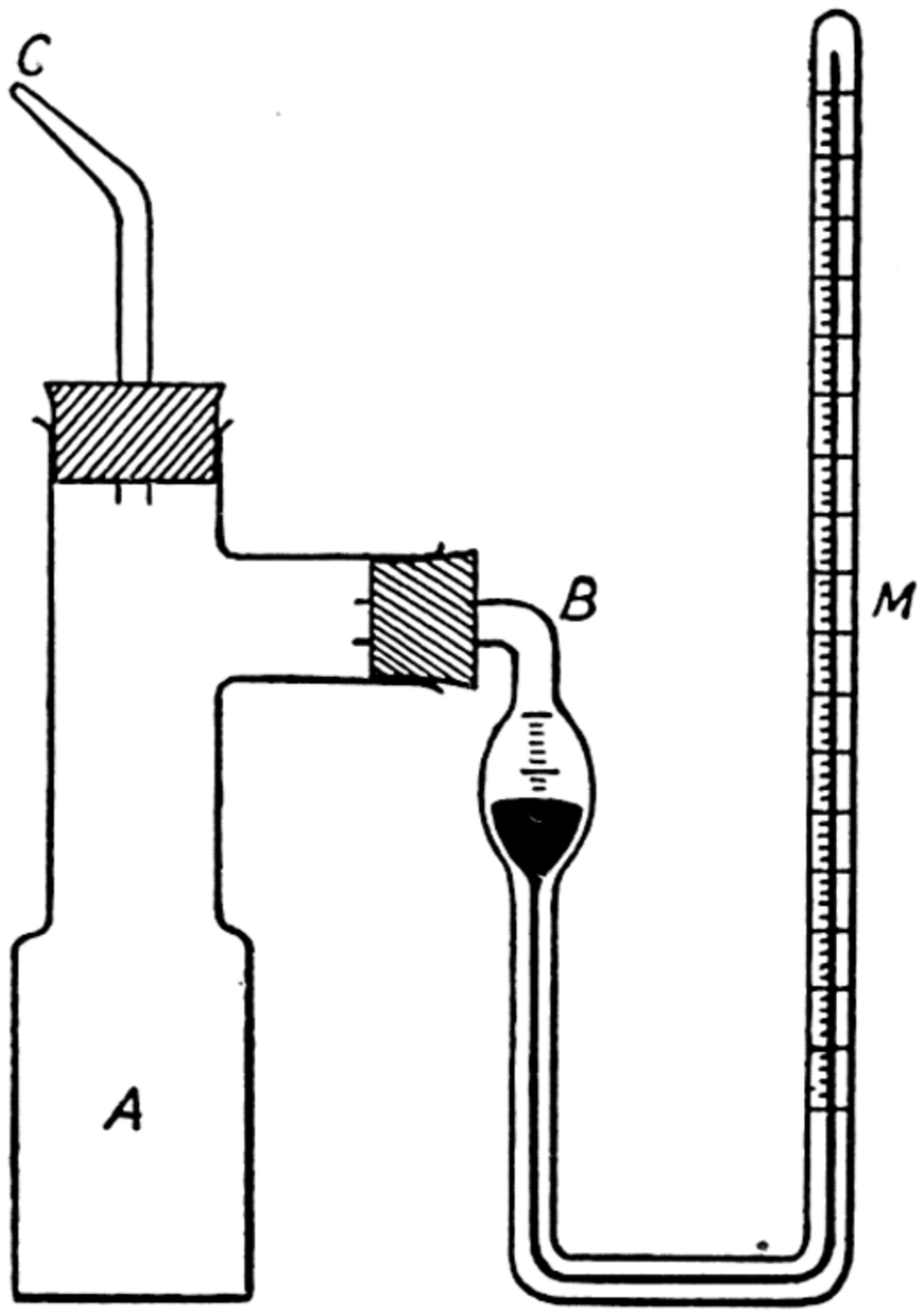


FIG. 59. Pfeffer's Apparatus for the Measurement of Osmotic Pressure

The apparatus used by Pfeffer is shown diagrammatically in Fig. 59. The unglazed porous pot within the pores of which copper ferrocyanide has been precipitated, is shown at *A*. A mercury manometer *M*, filled with nitrogen, is connected by a side arm *B* to the porous pot *A*. The porous pot and the remaining space in the side tube not occupied by mercury is filled with the solution under examination and the glass tube *C* finally sealed off leaving no air in the porous pot. The assembly is then placed in water maintained at a constant temperature until a constant pressure is indicated by the mercury manometer when the osmotic pressure is determined from the manometer reading. Pfeffer's technique in a somewhat elaborated form was also employed by Morse and Frazer (1901–23).

A somewhat different method for the measurements of osmotic pressure was introduced by the Earl of Berkeley and Hartley (1906–9). The apparatus these workers employed is shown diagrammatically in Fig. 60. Tube *A* is an open-ended

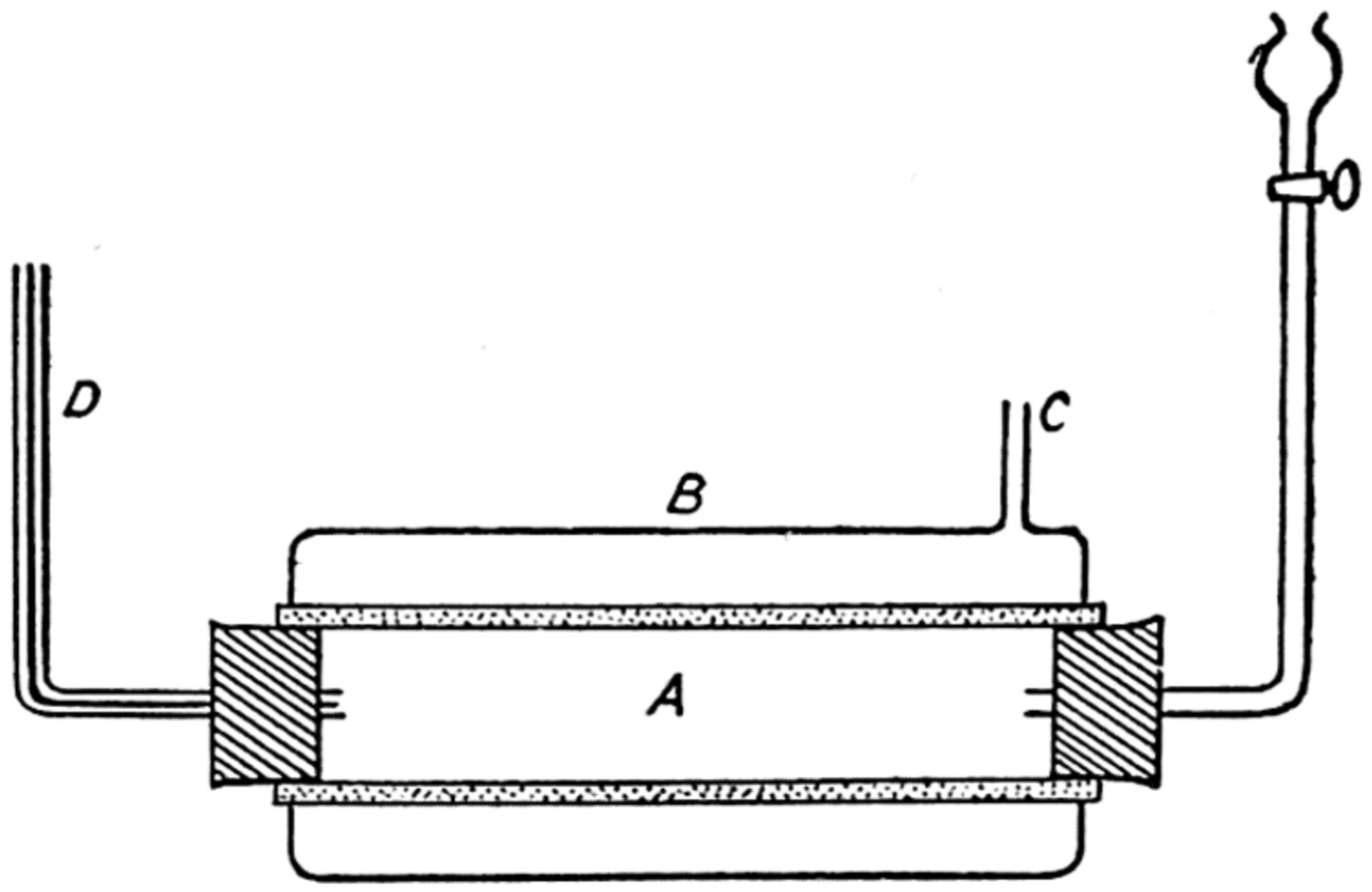


FIG. 60. Apparatus used by Berkeley and Hartley to Measure Osmotic Pressure

porous tube with a copper ferrocyanide membrane precipitated within its walls. After fixing tube *A* with liquid-tight joints in an enclosing bronze vessel *B*, tube *A* is filled with the pure solvent. The solution under investigation is contained within the bronze vessel *B*. A hydrostatic pressure is applied to the tube *C* and the direction of flow of solvent observed by noting the liquid level in the capillary tube *D*. Two pressures were determined, one which just permits a slow flow of solvent into the solution, the other—a higher pressure—which just allows the flow of solvent from the solution. The mean of these two pressures is taken as the osmotic pressure of the solution.

Influence of Concentration and Temperature upon Osmotic Pressure

Van't Hoff (1886) pointed out that a close parallel exists between the osmotic pressure of a solution and the pressure of a gas.

Influence of Concentration. The osmotic pressure of a solution is directly proportional to the concentration of the solution, and therefore varies inversely as the volume of the solution.

Table 27 gives some results for cane sugar solution.

TABLE 27

Osmotic Pressure of Cane Sugar Solutions at 0°*C*

Concentration (g/litre)	Osmotic Pressure, P' (atmospheres)	Volume of Solution V, containing one gramme molecular Weight of Cane Sugar (litres)	$P'V$
2·02	0·134	169·3	22·7
10·00	0·66	34·2	22·6
20·00	1·32	17·1	22·6
45·00	2·97	7·60	22·6
93·75	6·18	3·65	22·5

Boyle's Law may be expressed mathematically as

$$PV = \text{a constant} \quad . \quad . \quad . \quad . \quad (15)$$

This law may be extended to include solutions since, as is shown above in Table 27, the product of the osmotic pressure and the volume of solution containing one gramme molecular weight of the solute is of a constant value.

Influence of Temperature. The influence of temperature is illustrated by Table 28.

TABLE 28

Influence of Temperature upon Osmotic Pressure

Temperature (T)		Osmotic Pressure (P') (mm of mercury)	P'/T
(°C)	(°K)		
6·8	279·8	505	1·80
13·7	286·7	525	1·83
22·0	295·0	548	1·85
32·0	305·0	544	1·79
36·0	309·0	507	1·83

From this table it is clear that the osmotic pressure increases with rising temperature. The proportionality of osmotic pressure to the absolute temperature is indicated by the constancy of the ratio, osmotic pressure/absolute temperature, as given in the last column in the above table.

Since in the case of dilute solutions the osmotic pressure is proportional to the concentration of the solution, and also to its absolute temperature, these two statements may be combined, as in the case of gases, so that—

$$P'V = RT \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where P' = osmotic pressure of the solution, V = volume of solution (in litres) containing one gramme molecular weight of solute, R = gas constant (0·0815 litre-atmosphere), and T = temperature of solution on the absolute temperature scale; or, expressed in words—

The osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature, and occupying the same volume as the solution.

From this statement may be deduced the fact that *the gramme molecular weight of a solute is that weight which when dissolved in* 22·4 *litres of solution at* 0°*C will cause the solution to exhibit an osmotic pressure of one atmosphere.*

It also follows, by analogy with Avogadro's Hypothesis, that equal volumes of solutions which at the same temperature exhibit the same osmotic pressure contain the same number of solute molecules. Solutions exhibiting the same osmotic pressure are said to be *isotonic*. Thus, as described earlier, if red blood corpuscles are placed in distilled water they swell and finally burst; but if instead they are placed in normal saline solution (0·91 per cent sodium chloride solution) the red corpuscles neither swell as when placed in distilled water, nor shrink as when placed in strong sodium chloride solution, because the normal saline solution and the solution within the corpuscles are isotonic.

When, as a result of osmosis, a cell suffers shrinkage, this phenomenon

is termed *plasmolysis*, and the cell is said to be *plasmolyzed*. It should be noted here that the generalizations given above are not confined to those substances capable of volatilization at the temperature of the solution; they apply to all solutions although they are subject to the limitations that the total volume of solute molecules must be small compared with the volume of the solution. In the case of concentrated solutions deviations occur from this generalization just as gases at high pressures do not conform exactly to the gas laws.

Relationship of Osmotic Pressure and Vapour Pressure

Van't Hoff showed that the lowering of the vapour pressure of a solution is related directly to its osmotic pressure. This relationship may be deduced as follows. The beaker *B* (Fig. 61) which contains pure solvent is confined at a constant temperature within a bell-jar *A*. Into the solvent dips an inverted thistle funnel *D*, the end of which is closed by a semipermeable membrane *C*; the thistle funnel is filled with the solution under investigation. The bell-jar is evacuated. As a consequence of its osmotic pressure, the solution takes up solvent via the semipermeable membrane until the hydrostatic pressure due to the column of liquid *D* is equal to the osmotic pressure acting in the reverse direction. When this obtains, the vapour pressure of the solution p must be in equilibrium with that of the solvent p_0, that is, the difference between the vapour pressures at the levels *E* and *F* must be equal to the hydrostatic pressure of a column of vapour of height h, that is, the height of the column of liquid within the tube *D*.

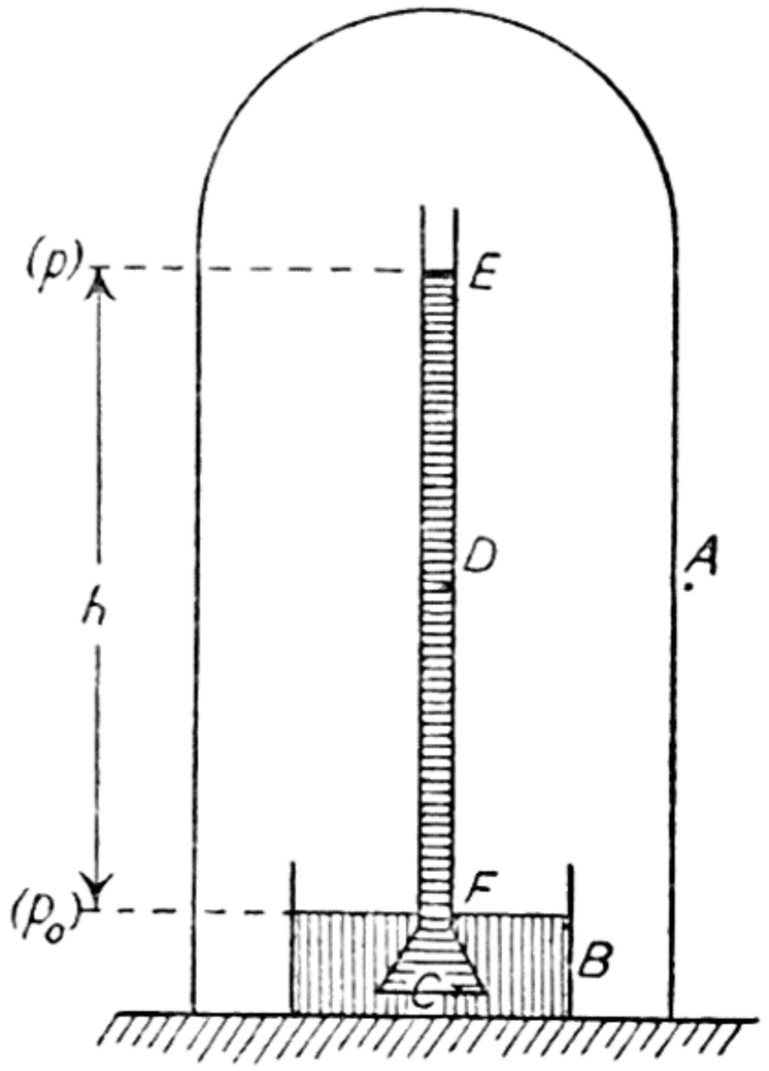


FIG. 61. Vapour Pressure and Osmotic Pressure of a Dilute Solution

In other words—

$$p_0 - p = \Delta p = hd \quad . \quad . \quad . \quad . \quad (17)$$

where d = density of the vapour.

If the molecular weight of the solvent be M, then the volume occupied by M g of solvent vapour at pressure p_0 and the absolute temperature T is given by—

$$V = \frac{RT}{p_0} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Therefore, since density is mass per unit volume—

$$d = \frac{M}{V} = \frac{Mp_0}{RT} \quad . \quad . \quad . \quad . \quad (19)$$

where d = density of the vapour, V = volume of the vapour, p_0 = pressure of the vapour, R = gas constant, and T = absolute temperature of vapour.

Assuming that the density of a dilute solution to be that of the pure solvent S, then the osmotic pressure of the solution P' is given by the equation (20).

$$P' = hS \text{ or } h = \frac{P'}{S} \quad . \quad . \quad . \quad . \quad (20)$$

But, from (17), $\Delta p = hd$

Therefore, introducing in (17) the values for d and h as given by (19) and (20) respectively—

$$\Delta p = \frac{P'Mp_0}{SRT} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

which may be rewritten—

$$\frac{\Delta p}{p_0} = \frac{MP'}{SRT} \quad . \quad . \quad . \quad . \quad . \quad (22a)$$

or,

$$P' = \frac{\Delta pSRT}{p_0 M} \quad . \quad . \quad . \quad . \quad (22b)$$

The accuracy of equation (22b) may be tested by comparison of the measured osmotic pressures with values calculated from vapour pressures. This is illustrated by the data in Table 29.

TABLE 29

Observed and Calculated Osmotic Pressures for Sugar Solutions at 30°*C*

Concentration of Solution (Moles per 1000 g of Solution)	Osmotic Pressure (atmospheres)	
	Observed	Calculated
0·1	2·47	2·47
1·0	27·22	27·0
2·0	58·37	58·5
3·0	95·16	96·2
4·0	138·96	138·5
5·0	187·3	183·0

But since in the case of dilute solutions,

$$\frac{\Delta p}{p_0} = \frac{n_2}{n_1 + n_2} \quad . \quad . \quad \text{from Eq. (2)}$$

which may be simplified for dilute solutions, thus,

$$\frac{\Delta p}{p_0} = \frac{n_2}{n_1} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where n_1 and n_2 are the number of moles of solvent and solute respectively, therefore, from (22a),

$$\frac{\Delta p}{p_0} = \frac{n_2}{n_1} = \frac{MP'}{SRT}$$

And since,
$$V = \frac{M}{S} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

then,
$$P'V = \frac{n_2 RT}{n_1} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

The ratio n_2/n_1 is the number of moles of solute per mole of solvent, so that

$$P'V = n_2 RT \; . \quad . \quad . \quad . \quad . \quad (26)$$

which is an equation analogous to the simple gas law equation.

Determination of Molecular Weight from Osmotic Pressure Measurements. It has been established (equation (26)) that

$$P'V = n_2 RT$$

But,
$$n_2 = \frac{w}{M} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where w = weight of solute in V litres of solution, and M = molecular weight of solute.

Therefore,
$$P'V = \frac{wRT}{M} \quad . \quad . \quad . \quad . \quad (28)$$

and,
$$M = \frac{wRT}{P'V} \quad . \quad . \quad . \quad . \quad (29)$$

From this expression the molecular weight of the solute may be evaluated, knowing that the gas constant $R = 0{\cdot}0815$ litre-atmospheres, and the numerical values of w, T, P' and V as observed data.

On account of the difficulty of measuring osmotic pressures this method has only found application in a limited field, namely for those substances of very high molecular weight, e.g. proteins, high polymers having molecular weights of 100 000 or more, and carbohydrate derivatives.

Review of Methods for Determining Molecular Weights in Solution. Although all the methods described previously in this chapter may be employed to determine within 5 per cent or less the true molecular weight

of substances which cannot be vaporized without undergoing decomposition, that method involving measurements of the depression of the freezing point is generally preferred, firstly because such determinations are more easily made, and secondly because this method gives the most accurate results. Using Beckmann's method results may easily be obtained within 1 per cent of the theoretical value. In connexion with this particular method it is important that there must not be too great an undercooling, nor must the solvent and the solute be capable of forming solid solutions; in addition the solutions investigated should be dilute.

Abnormal Molecular Weights

In spite of taking the precautions just enumerated, abnormal values are obtained for the molecular weights in the case of certain solutes. Such abnormalities may be caused by the phenomena either of (*a*) association, or (*b*) dissociation.

Association. Certain substances give values for molecular weights in solution which are higher than the true molecular weights. Thus, acetic acid in benzene has a molecular weight of 120 instead of 60 as calculated from the formula, CH_3COOH. Measurements of the freezing point of acetic acid solutions in water give for the acid the normal molecular weight of 60.

In such cases as this it is considered that a condition of equilibrium exists between the simple and complex molecules of the acid thus,

$$\underset{\text{(associated state)}}{(CH_3COOH)_2} \rightleftharpoons \underset{\text{(normal state)}}{2CH_3COOH}$$

and this equilibrium is influenced by the solvent, the concentration of the solute and the temperature. This view is supported by the fact that in the region of its boiling point the vapour density of acetic acid is much greater than its normal value (i.e. 30); in other words, the vapour would appear to be in the "associated" state. This phenomenon is termed *association*.

Dissociation. In contrast to compounds such as acetic acid, which is associated in benzene, most salts in aqueous solution give values for the molecular weights which are lower than those calculated from the formulae of these compounds. This fact is due to the *ionic dissociation* which these compounds undergo on dissolving in water.

Although potassium chloride in the crystalline state is made up of a rigid assembly of potassium and chlorine ions, on dissolving in water these ions are no longer held in position since the attractive forces between neighbouring ions have been weakened by the water. Thus, more and more ions tend to move apart from one another into the solution in a haphazard, unpartnered manner the more diluted the solution becomes. This may be represented thus—

$$KCl \rightleftharpoons K^+ + Cl'$$

The magnitude of the dissociation of the solute, that is, the degree of dissociation, may be evaluated in a manner similar to that employed to determine the degree of thermal dissociation (*see* p. 31). The following example will help to make clear the method of calculation involved.

The molecular weight of potassium chloride as determined by measurements of the freezing point of an aqueous solution of this salt was 41·4. Calculate the degree of dissociation of this salt.

Suppose that there are n molecules of potassium chloride and that the fraction of each molecule which undergoes dissociation is α, then in the equilibrium condition there will be $n(1-\alpha)$ molecules of undissociated potassium chloride and $n\alpha$ ions of the potassium and chlorine ions respectively.

$$\underset{n(1-\alpha)}{KCl} \rightleftharpoons \underset{n\alpha}{K^+} + \underset{n\alpha}{Cl'}$$

Reduced to its lowest terms this equation is—

$$\underset{(1-\alpha)}{KCl} \rightleftharpoons \underset{\alpha}{K^+} + \underset{\alpha}{Cl'}$$

Thus, the total number of particles present is $1 + \alpha$.

Now, $$\frac{\text{Observed molecular weight}}{\text{Theoretical molecular weight}} = \frac{1}{1+\alpha}$$

Introducing data from formula

$$\frac{41{\cdot}4}{74{\cdot}55} = \frac{1}{1+\alpha}$$

and, $$\alpha = 0{\cdot}799$$

CHAPTER 9

PHASE EQUILIBRIA

LEADING on from the discussion in the last chapter of dilute solutions and their colligative properties, it is the intention in the present chapter to discuss (*a*) the properties of solutions of volatile substances, and (*b*) concentrated solutions in general, for which purpose use will be made of the phase rule and the distribution law.

SOLID-LIQUID-VAPOUR EQUILIBRIA

In Fig. 62, the curves *OA* and *OB* depict the variation with temperature of the vapour pressure of the liquid and the solid forms respectively of a given substance. It will be observed that curve *OA* only extends as far as the critical point, but curve *OB* may be continued to the absolute zero. Curve *OA* corresponds to the equilibrium conditions of temperature and pressure for a system of liquid and vapour, whilst *OB* similarly corresponds to the conditions of temperature and pressure under which a system of solid and vapour are in equilibrium.

The point *O* at which these two curves intersect must be the point at which the three physical states of the substance—solid, liquid and gaseous —may co-exist; hence, the point *O* is known as the *triple point.*

The influence of pressure on the melting point of the solid is indicated by the curve *OC*. (It should be noted that the slope of *OC* is grossly exaggerated for the purpose of clarity.) Thus, *OC* depicts the temperatures and pressures at which the solid and liquid phases may exist in equilibrium.

In Fig. 62 the effect of increase in pressure is shown as lowering the melting point of the solid, as, for example, in the case of water. The curve *OC* intersects the curves *OA* and *OB* at the triple point *O* where all three phases may co-exist. In the case of water, the triple point is at a temperature of + 0·0075°C, and a pressure of 4·58 mm of mercury.

From curve *OB* it will be noted that if vapour at some pressure below that of the triple point is chilled sufficiently it will be possible to condense the vapour directly to solid without forming liquid as an intermediate stage. This represents the condition under which snow and hoar frost are produced in the upper atmosphere, and on the ground, respectively. For this reason the vapour pressure curve of ice *OB* is sometimes termed the "hoar frost" curve. In a similar manner *flowers of sulphur* are formed by the condensation on a cold surface of sulphur vapour the pressure of which is maintained below that of the triple point (*see* Fig. 65).

Just as vapour may be converted directly to solid, so conversely a solid may be completely vaporized without the production of the intervening liquid phase provided that the pressure of the vapour is not allowed to exceed that of the triple point.

If the vapour pressure of a solid is higher than that of the atmosphere it is readily possible to purify it by making use of a process depending

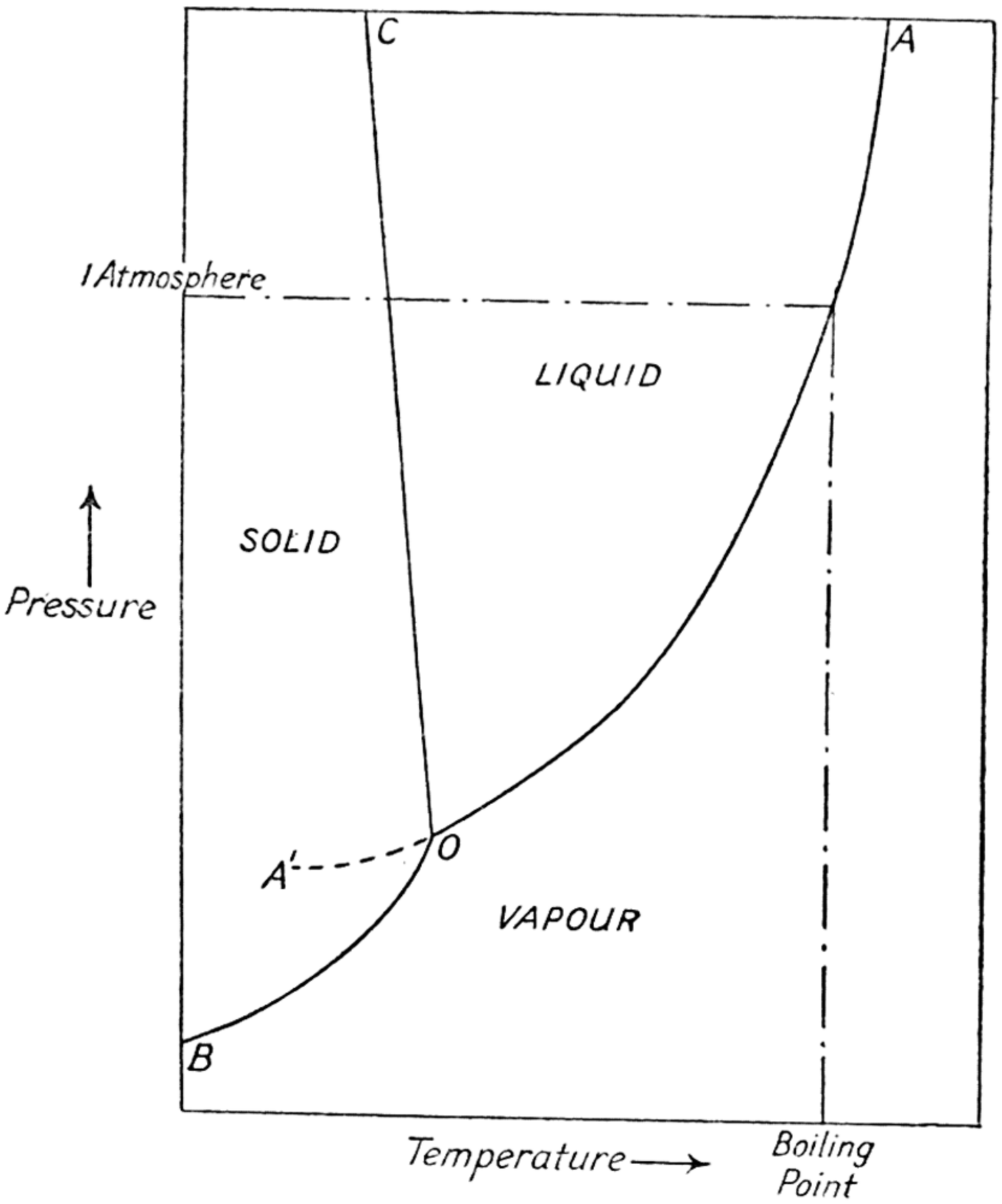


FIG. 62. Solid-liquid-vapour Equilibria

upon the principles just described; this process is known as *sublimation*. In the case of iodine, the temperature of the critical point is 114·15°C, when the equilibrium pressure is 90·0 mm of mercury. Thus, if iodine is heated to some temperature below 114·15°C, it will vaporize without melting, and if the vapour is condensed on a cool surface the pressure will be maintained below 90 mm so that vaporization of the whole of the solid will occur. Other substances capable of sublimation in a similar manner to iodine are benzoic acid and naphthalene.

Certain substances, however, have triple point pressures in excess of 1 atmosphere. Carbon dioxide is an example of such a substance for which

the triple point pressure is 5·11 atmospheres at — 56·4°C. Such a substance cannot be melted by heating at atmospheric pressure, since liquid carbon dioxide may only be formed if the pressure exceeds 5·11 atmospheres; at all pressures lower than this value the solid passes directly into the gas.

The diagram shown in Fig. 62 is termed a "phase diagram" or an "equilibrium diagram." By means of phase diagrams a great deal of valuable information may be obtained; for example, suppose the pressure of a system remains at a constant value above the triple point whilst the temperature is progressively raised it will be evident that the whole of the substance will ultimately be converted from the solid to the liquid state. Similarly, if, whilst the temperature is maintained at a constant value, the pressure is progressively reduced, it will be obvious that complete vaporization will ultimately occur. Thus, the phase diagram may be divided into three areas, each occupied by a single, stable phase—the solid, the liquid, and the gaseous phases respectively. Two phases may co-exist under the conditions of temperature and pressure given by any one of the lines *OA*, *OB* and *OC*, but the three phases may only co-exist at one specific temperature and pressure—the triple point.

It is sometimes possible to cool a liquid below its freezing point without solidification occurring; this is termed *supercooling* or *undercooling*. This phenomenon is represented by the line *OA′* along which the liquid-vapour system exists in a condition of metastable equilibrium. The addition of a small amount of the solid phase to the liquid-vapour system results in the immediate solidification of all of the liquid phase.

From Fig. 62 it will be noted that the metastable system exhibits a higher vapour pressure than the stable system at the same temperature; this is always the case and indicates the tendency for the metastable system to pass into the stable system.

Effect of Polymorphic Changes on Phase Diagrams

As stated earlier, a number of substances, both elements as well as compounds, exist in polymorphic forms. Each of such polymorphic forms has its own characteristic vapour pressure, and two general types of vapour pressure-temperature relationships may be distinguished according as to whether the substance in question exhibits either monotropy or alternatively enantiotropy.

Discussing first the case of a monotropic substance—suppose it is the α-form which is stable whilst the β-form is the metastable form. The vapour pressure-temperature curve for the α-form is depicted as *AB* (Fig. 63), whilst that of the β-form is shown as the curve *DE*. The metastable β-form will tend to transform into the stable α-form as is indicated by the fact that the former has a higher vapour pressure at all temperatures. The curve *BC* represents the vapour pressure-temperature relationship for the liquid, whilst the point *B* is the triple point at which the α-form, the

liquid and the vapour co-exist in equilibrium. The point E is the melting point, at its own vapour pressure, of the metastable β-form.

An extension of the curves, AB and DE, may be made to a point of intersection F which is the hypothetical transition temperature, but in reality the point F has no significance since it is above the melting points of the two forms.

A stable substance does not transform spontaneously into a metastable substance and in order to obtain the β-form from the α-form it is necessary either to melt or to vaporize the latter and rapidly chill the liquid or the vapour obtained. By rapidly chilling the liquid, the system passes down

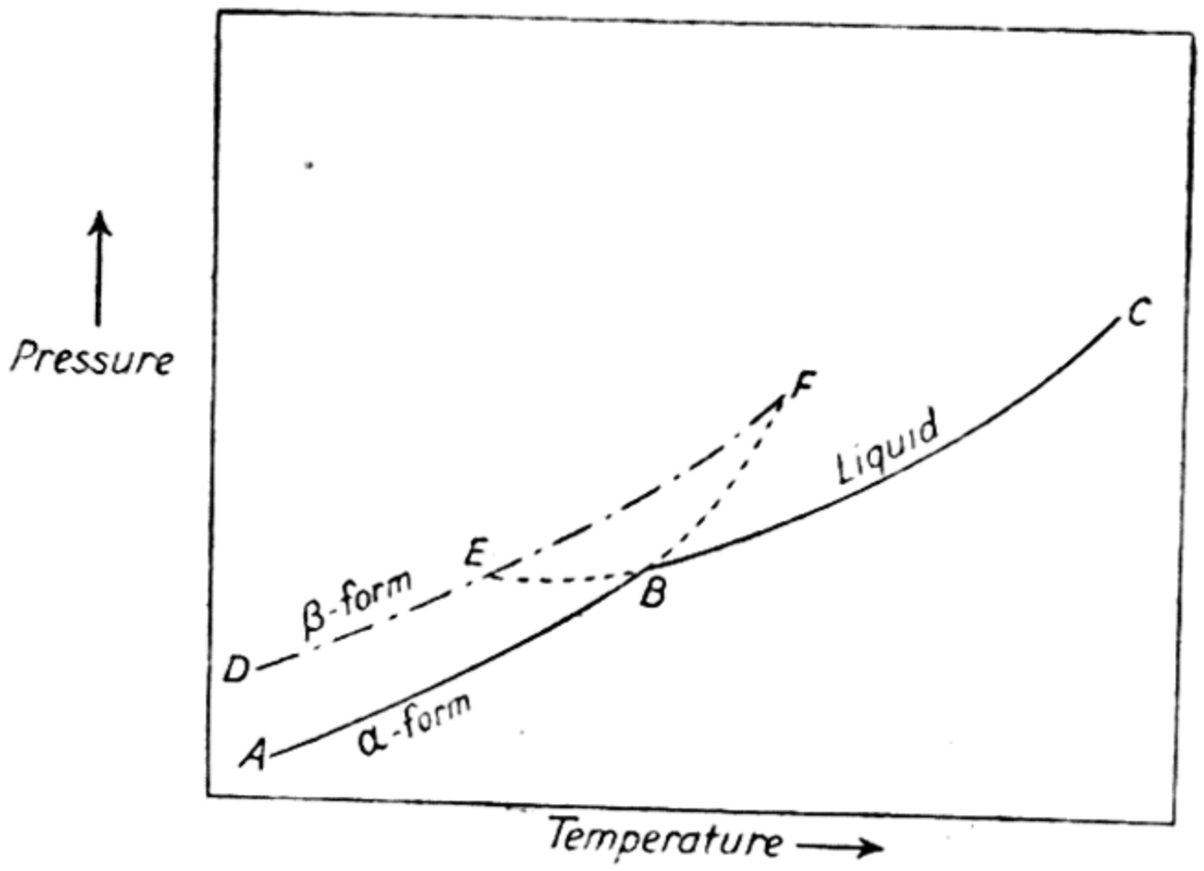


FIG. 63. Vapour Pressure—Temperature Relationship of Monotropic System

the metastable curve BE and crystals of the β-form separate out at the point E.

In the case of an enantiotropic substance, suppose that the two forms are designated α and β respectively, the former being the stable form below the transition temperature whilst the β-form is stable above the transition temperature. The vapour pressure-temperature curves for two such enantiotropic modifications are depicted in Fig. 64 in which AB represents the α-form and BC the β-form, whilst CD is the vapour pressure-temperature curve for the liquid phase. If the α-form is heated slowly the vapour pressure increases, as indicated by the curve AB, until at B the α-form transforms to the β-form, the vapour pressure then increases as shown by BC until the β-form melts at the pressure and temperature of the triple point C.

On the other hand, however, if the α-modification is heated rapidly this form may exist, although in a metastable condition, above the temperature of the point B, following without a break the curve BE which is a continuation of the curve AB, until the metastable triple point E is reached. From E to C the vapour pressure curve is a continuation of the curve CD.

Likewise, if the liquid is rapidly chilled, supercooling may occur down to the point E when the α-form commences to crystallize.

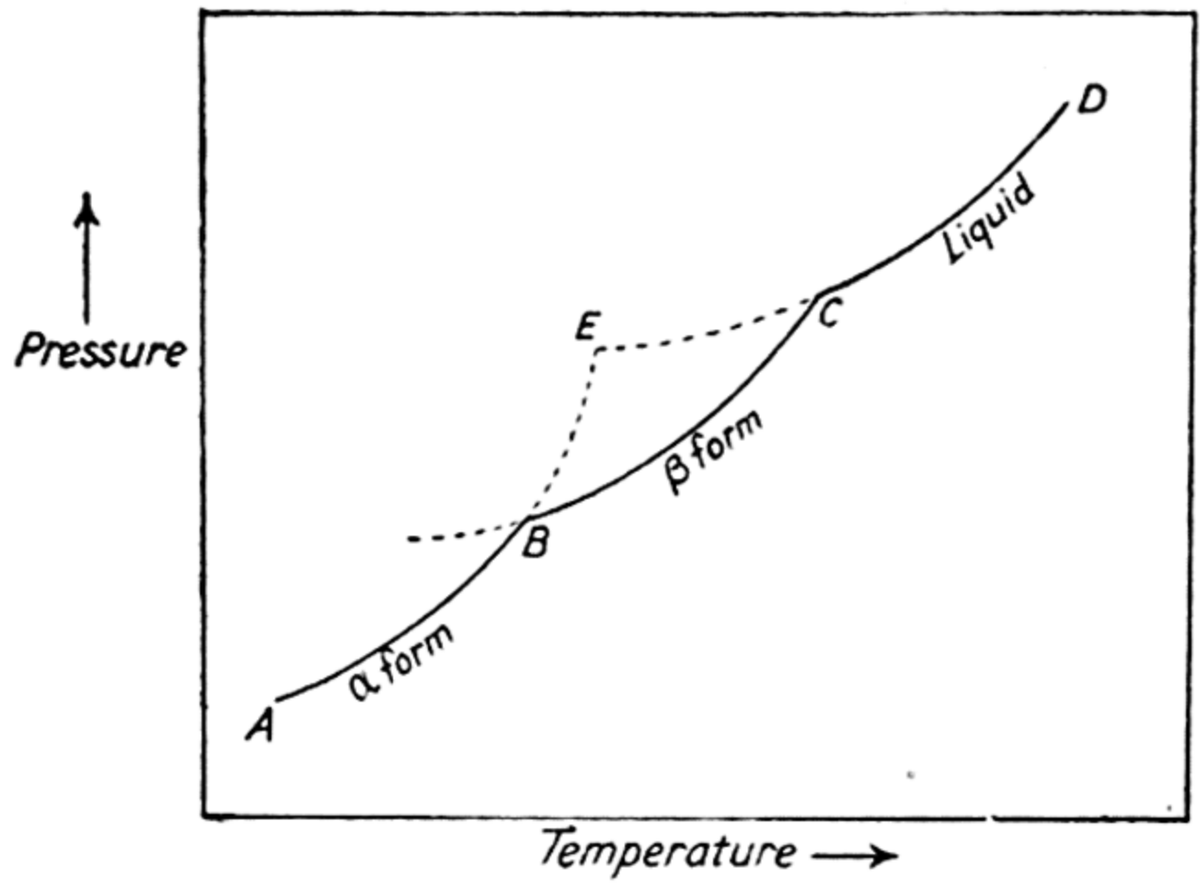


FIG. 64. Vapour Pressure—Temperature Relationship of Enantiotropic System

From a study of curves of the types shown in Fig. 64 an explanation may be obtained of the experimental observations that enantiotropic substances such as sulphur and tin melt at different temperatures according to the rapidity with which such substances are heated.

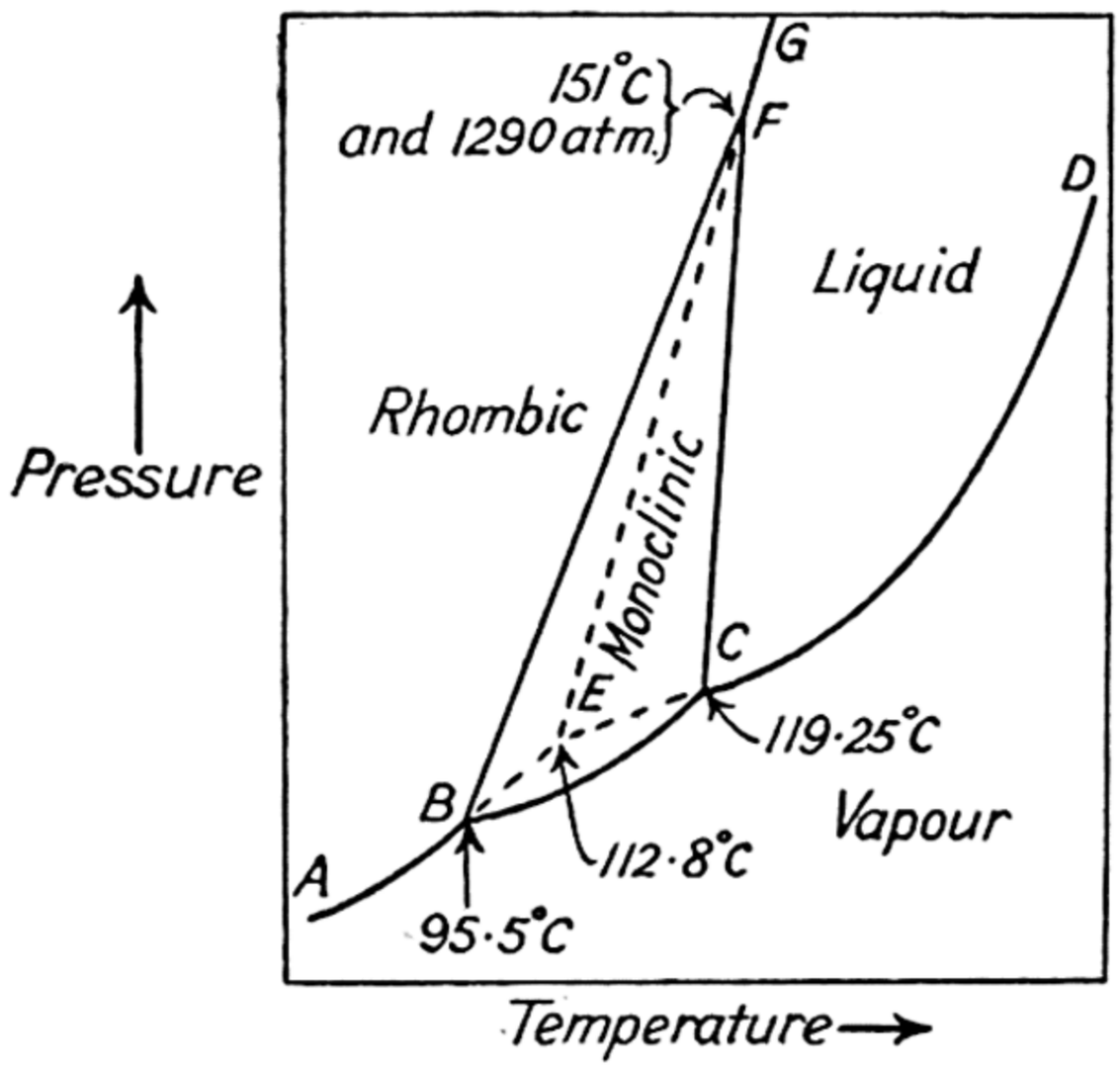


FIG. 65. Phase Diagram for Sulphur

The Sulphur System. The phase diagram for sulphur is shown in Fig. 65 in which curves are included for the enantiomorphic rhombic and monoclinic forms. AB is the vapour pressure curve for the rhombic form, and BC is the curve for the monoclinic form; the melting point of rhombic sulphur is at E (112·8°C) which may only be attained if rhombic sulphur

is rapidly heated so that the transition to monoclinic sulphur does not occur. Curve *BF* depicts the influence of pressure on the transition point of rhombic sulphur to monoclinic sulphur, whilst *CF* depicts the influence of pressure upon the melting point of monoclinic sulphur. The metastable curve *EF* depicts the influence of pressure upon the melting point of rhombic sulphur.

Thus, this diagram exhibits four triple points, as shown in the following table.

Triple Point	Phases in Equilibrium
B	Rhombic sulphur Monoclinic sulphur Sulphur vapour
C	Monoclinic sulphur Liquid sulphur and sulphur vapour
E	Rhombic sulphur Liquid sulphur and sulphur vapour
F	Rhombic sulphur Monoclinic sulphur Liquid sulphur

It should be noted that the pressure at the triple point *F* is very high so that in Fig. 65 the slopes of the lines *BF* and *CF* have been exaggerated very considerably in order to bring *F* on to the diagram.

THE PHASE RULE

When studying equilibrium diagrams such as those described above, the generalization known as the Phase Rule is often of considerable value. The phase rule was deduced from thermodynamic data by J. Willard Gibbs (1876), but its application to physical chemistry is chiefly due to H. W. B. Roozeboom (1884).

The terms employed in the phase rule will be explained before the rule itself is stated; these terms are four in number—a system, a phase, a component, and degree of freedom.

A *system* is a mass of material, solid, liquid or gaseous, or a mixture of these three states. It consists of one or more constituents each of which is a definite, separate and homogeneous substance. Each of these separate and homogeneous substances separated from other parts of the system by a bounding face is termed a *phase*. In many cases a phase is an element,

but it need not always be so; it may be a chemical compound or a solid solution. Thus ice, water and water vapour are three phases. A solution of ethyl alcohol and water, since they are completely miscible in one another constituting a single liquid solution, is a single phase. On the other hand, water and ether are not so perfectly miscible as water and ethyl alcohol, so that when water and ether are allowed to mix they form two layers, and since there is a definite bounding face between these two layers, water and ether constitute two phases. In a gas or a mixture of gases, the intimate mixing of the molecules renders it homogeneous and such a system always constitutes a single phase.

The simple substances from which phases can be built are known as *components*, the number of components being the smallest number of such substances from which the phases can be made. Thus, in the ice-water-water vapour system there is one component, namely water, H_2O. The phase rule, however may be applied to more complex systems, for example in the equilibrium—

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)^* \quad . \quad . \quad (1)$$

there are three phases, solid $CaCO_3$, solid CaO and gaseous CO_2, and this system has two components which may be any two of the phases involved in the equilibrium. The dissociation of any carbonate, oxide or similar compound involves two components. In the following equilibrium, however, there are three components

$$Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g) \quad . \quad . \quad (2)$$

A system may be subjected to variation by three variable factors, pressure, temperature and concentration, that is, the relative amounts of components (*not* phases) present.

The relationship between these variables, the components and the phases for a system in equilibrium, may be stated in mathematical form, thus—

$$F = C - P + 2 \quad . \quad . \quad . \quad . \quad (3)$$

where F = number of degrees of freedom, C = number of components, and P = number of phases.

This is the mathematical expression of the Phase Rule.

SOLUTIONS OF GASES IN LIQUIDS

Gases are only partially soluble in liquids, the actual value of the solubility being dependent upon the chemical characteristics of the gas and the solvent, and upon the temperature and the pressure of the gas. The Phase Rule shows that for a system consisting of a gas and a liquid solvent

* The suffixes (*s*), (*g*) and (*l*) refer to the solid, gaseous and liquid states respectively of the compounds or elements whose formula is stated immediately before the suffix.

there are two components and two phases, and the number of degrees of freedom are given by—

$$\begin{aligned} F &= C - P + 2 \\ &= 2 - 2 + 2 \\ &= 2 \end{aligned}$$

Thus, for the equilibrium constant to be completely defined the two variables, temperature and pressure must be fixed.

The solubility of a gas in a liquid is usually expressed as the *absorption coefficient*. The absorption coefficient (as proposed by R. Bunsen) of a gas with respect to a given liquid is the volume of the gas reduced to S.T.P. which dissolves in unit volume of the liquid at the temperature of the determination, under a partial pressure of one atmosphere, or mathematically—

$$\alpha = v_0 / V_p \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where α = absorption coefficient, v_0 = volume of the gas dissolved, reduced to S.T.P., V = volume of the solvent, and p = partial pressure of the gas in atmospheres.

The absorption coefficients of some of the more common gases in water and in some non-aqueous solvents are given in Table 30.

TABLE 30

Absorption Coefficients of some Common Gases at 20°C

Solvent	H_2	He	N_2	O_2	CO	CO_2	H_2S	NH_3	HCl
Water . . .	0·017	0·009	0·015	0·028	0·025	0·88	2·68	710	442
Carbon disulphide .	0·031	—	0·049	—	0·076	0·83	—	—	—
Chloroform . .	—	—	0·120	0·205	0·177	3·45	—	—	—
Ethyl alcohol . .	0·080	0·028	0·130	0·143	0·177	3·0	—	—	—
Acetone . . .	0·065	0·030	0·129	0·207	0·198	6·5	—	—	—
Di-ethyl ether . .	0·12	—	0·24	0·415	0·38	5·0	—	—	—
Benzene . . .	0·066	0·018	0·104	0·163	0·153	—	—	—	—

Influence of Temperature

In general when gases dissolve in water there is a liberation of heat, and it follows, therefore, from a consideration of Le Chatelier's principle (*see* p. 224), that a rise of temperature will lead to a decrease in solubility. This is the reason why in many cases gases are readily removed from solution by boiling. This ready removal of gas from a boiling solution occurs because the gas diffuses into the bubbles of vapour which are removed more rapidly than the liquid is itself vaporized. A similar effect may be

produced at ordinary temperatures by bubbling a sparingly soluble, and chemically indifferent gas through the solution. Thus, ammonia in water may be removed by bubbling air through the solution; the same effect is obtained, although a much longer time is required, by leaving the solution exposed to the atmosphere. Likewise, with the object of removing dissolved hydrogen from molten aluminium-base light alloys prior to casting it is customary to degasify by bubbling a stream of chlorine and/or nitrogen through the molten alloy. If this degasification were not carried out the dissolved hydrogen would pass out of solution when the alloy solidified, giving rise to a type of defect known as "pinholing." Typical values for the absorption coefficients of some gases at different temperatures are given in Table 31.

TABLE 31

Variation with Temperature of Absorption Coefficients of some Common Gases

(*Water the solvent in each case*)

Gas	Temperature (°C)			
	0	15	60	100
Ammonia . .	1300·0	802·0	—	195·0
Hydrogen chloride .	506·0	458·0	339·0	—
Carbon dioxide .	1·713	1·019	0·360	—
Oxygen . . .	0·049	0·034	0·020	0·017
Nitrogen . . .	0·024	0·018	0·010	0·010
Hydrogen . .	0·022	0·019	0·016	0·016
Argon . . .	0·058	0·040	—	—

From Table 31 it will be noted that the relative influence of temperature variation is greater for gases like ammonia, hydrogen chloride and carbon dioxide, than for the sparingly soluble gases such as nitrogen and hydrogen. This implies that greater heats of solution obtain in the former cases; and this fact is very likely related to the fact that chemical combination occurs between the gas and water in these cases.

Influence of Pressure

The solubility of a gas in a liquid is profoundly affected by variation in the pressure of the gas. The quantitative relationship between pressure and solubility is expressed in Henry's Law, which states that *the mass of gas dissolved by a given volume of solvent at constant temperature is directly proportional to the pressure of the gas with which it is in equilibrium*, or expressed mathematically—

$$p/m = K \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where m = mass of gas dissolved by unit volume of solvent at equilibrium pressure p, and K = a constant.

Now, the mass m of gas dissolved by unit volume of solvent may be rewritten as grammes per millilitre of solvent, and this is proportional to the concentration expressed in molecules per litre of solvent, or per litre of solution, since the volume of the solvent suffers no large change when the gas dissolves. In addition, the pressure p of the gas is proportional to the number of molecules in the gas, and hence is also proportional to the concentration of molecules per litre of the gas phase.

Then, since
$$p/m = K \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{\text{Pressure of gas}}{\text{Weight of gas in grammes per millilitre of solution}} = \text{a constant (at constant temperature)} \quad . \quad (6)$$

And it follows that, independently of pressure

$$\frac{\text{Concentration of gas in gaseous layer}}{\text{Concentration of gas in solution}} = \text{a constant (at constant temperature)} \quad . \quad (7)$$

Equation (7) is a form of the important generalization known as the *Distribution Law* or the *Partition Law*.

Deviations from Henry's Law. Experimental results show that in the case of sparingly soluble gases, Henry's Law is obeyed in a satisfactory manner provided that the pressures are not too high, nor the temperatures too low. As was shown above, Henry's Law is one form of the Distribution Law, and in addition is related to Raoult's Law. Since such generalizations are strictly only applicable to ideal systems, any departure from ideal behaviour will lead to departure from Henry's Law. Deviations of this type are not unexpected at low temperatures and high pressures, particularly in the case of readily liquefiable gases.

In addition to these reasons for deviation from Henry's Law, there is also the possibility of compound formation between the solvent and the gas. Thus, for example, ammonia exhibits considerable deviation from Henry's Law.

Solubility of a Mixture of Gases. If a mixture of sparingly soluble gases is brought into contact with a liquid and the system allowed to attain equilibrium, it will be found that each of the gases present in the gaseous mixture will have dissolved in the solvent liquid, each gas according to its own partial pressure. This fact was discovered by John Dalton (1805).

Solubility of Gases in Aqueous Solutions. In general, gases exhibit a lower solubility in aqueous solutions of salts and other solid compounds than they do in pure water. The dissolved solid may be either an electrolyte, such as sodium chloride, or a non-electrolyte, such as sugar. This phenomenon is an example of the so-called "salting-out" effect. From

the experimental evidence available it would appear that the salting-out effect of an ion is larger the smaller its size and the greater its charge.

Determination of the Solubility of a Gas in a Liquid

Sparingly-soluble Gases. A measured volume of the gas under investigation at known temperature and pressure is confined within one limb of the gas burette *A* (Fig. 66). The absorption bulb *B* is weighed, first empty and

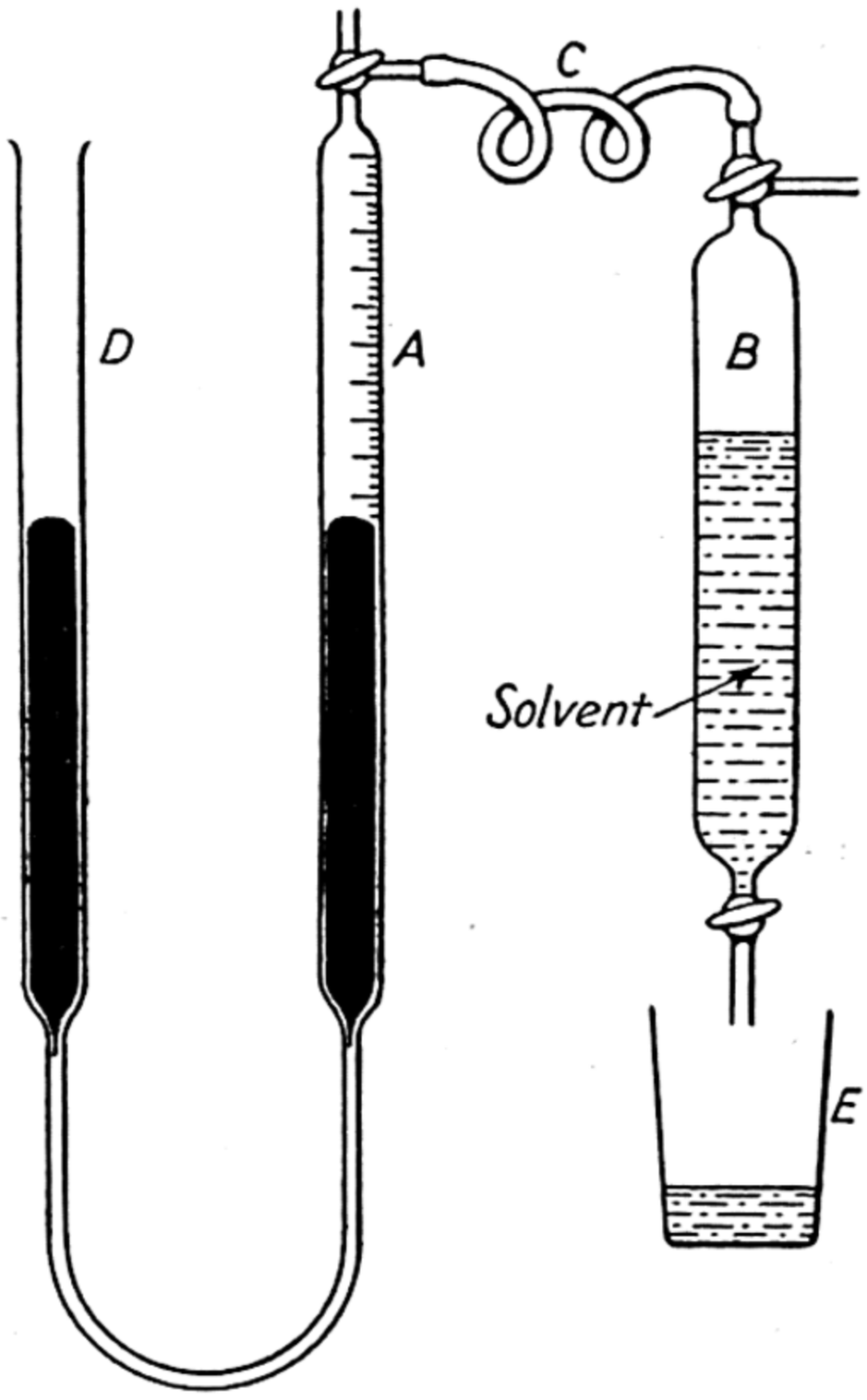


FIG. 66. Apparatus for Determining the Solubility of Sparingly-soluble Gases in Liquid Solvents

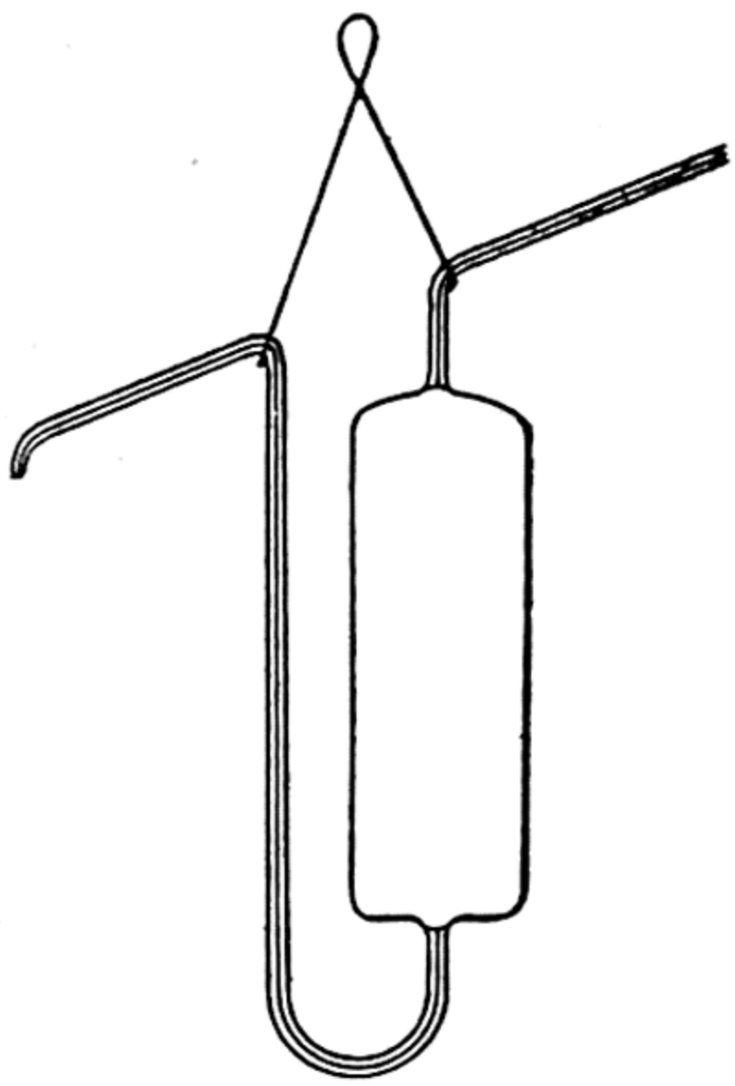


FIG. 67. Apparatus for Determining Solubility of very Soluble Gases in Liquid Solvents

then filled with solvent, and then attached to the burette *A* by means of a flexible tube *C*. Some solvent is then run off from the bulb *B* into a tared beaker *E*, and the gas confined within *A* transferred to bulb *B* by raising the levelling-tube *D*. Bulb *B* is then agitated, the connecting taps opened and the gas restored to atmospheric pressure by adjustment of the levelling-tube *D*. The absorption of the gas is allowed to continue until there is no further decrease in the volume of the gas in burette *A*. From the data obtained, the absorption coefficient may be evaluated.

Very Soluble Gases. For freely soluble gases a piece of apparatus known as a "pyknometer" is employed; this is shown in Fig. 67. In use the pyknometer is first weighed empty and then a few millilitres of the solvent

introduced. A current of the gas under investigation is then passed through the liquid to ensure that a saturated solution has been obtained. The apparatus is then sealed and re-weighed. The weight of the gas and liquid is then known and the amount of the dissolved gas determined by titration, for example, by standard alkali in the case of an acid gas, or by standard acid in the case of an alkaline gas.

SOLUTIONS OF LIQUIDS IN LIQUIDS

The behaviour of liquids towards one another gives rise to considerable variations in the solubilities of liquids in liquids. These variations are caused by the constituents of a liquid system differing in respect of (*a*) internal pressure, (*b*) polarity, (*c*) length of hydrocarbon chain or similar grouping, (*d*) association of one or other of the liquids, or (*e*) occurrence of compound formation between the component liquids. The internal pressure of a liquid is a measure of the attractive force existent between its molecules. Thus, when two liquids having internal pressures of similar magnitude are mixed they form a solution in which the internal pressures are almost unchanged; the closer the internal pressures of the individual liquids the closer will the solution approximate to an ideal solution, from the point of view of Raoult's Law. On the other hand should the respective internal pressures be different, the solution will diverge from ideal behaviour and such deviations will be positive in nature. The greater the difference of internal pressures, the greater the divergence of the solution from ideal behaviour.

The electrical character of the molecules may also give rise to deviation of the solution from ideal behaviour. Molecules are either polar (i.e. with a dipole moment), or non-polar (i.e. with no dipole moment). Polar liquids boil at relatively high temperatures and are not normally miscible with non-polar liquids since the mutual attraction of the polar molecules for one another is greater than their attraction for non-polar molecules. Water, which is probably the commonest example of a polar liquid, is only slightly miscible with the hydrocarbons. Polar liquids tend to form loose molecular groupings which give rise to the so-called "associated" liquids. Non-polar liquids, in general, have low boiling points and are capable of mixing freely with one another. The mixing of polar and non-polar liquids gives rise to positive deviations from ideal behaviour. Similarly, a solution of a long-chain solute dissolved in a simple solvent will also exhibit positive deviation from ideal behaviour. Such is the case when long-chain fatty acids or alcohols are dissolved in water. On the other hand, should compound formation occur between the constituent liquids the number of uncombined molecules will be less than would have been the case had this phenomenon not occurred, and the vapour pressure of the solution will be less than the theoretical value with the result that negative deviations occur.

Resulting from the effect of the factors discussed above, two liquids may be—

(i) Completely miscible in one another in all proportions,

(ii) Partially miscible in one another,

(iii) Immiscible in one another.

Two Liquids Completely Miscible in One Another in All Proportions. If a mixture of two liquids behaves in an ideal manner then the plot of the partial pressure of each constituent liquid against the composition of the liquid mixture will be a straight line passing through the origin as indicated

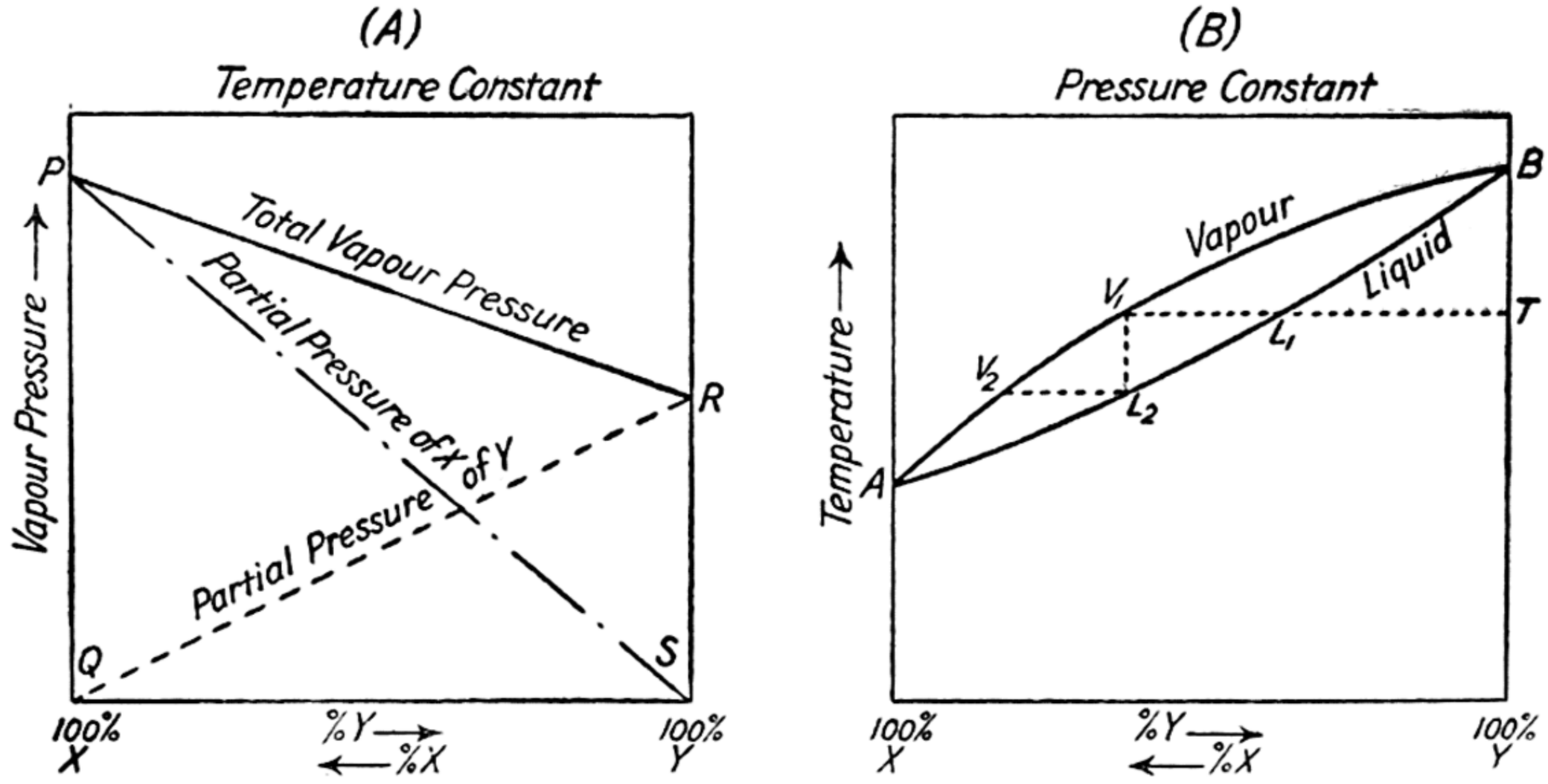


FIG. 68. Vapour Pressure—Composition and Temperature—Composition Curves with neither Minimum nor Maximum in Total Vapour Pressure Curve

by curves *QR* and *PS* (Fig. 68 at (*A*)). The total vapour pressure, that is, the sum of the partial pressures, will, therefore, also be a straight line as indicated by *PR*. There are, however, few pairs of liquids which behave in this ideal manner, most binary liquid mixtures exhibiting either positive or negative deviations for the reasons previously described.

From a study of total vapour pressure-composition diagrams three types of diagrams may be distinguished, they are—

Type A where the total vapour pressure curve is practically a straight line between the vapour pressures of the component liquids.

Type B where the total vapour pressure curve passes through a minimum value below the vapour pressures of the component liquids.

Type C where the total vapour pressure curve passes through a maximum value above the vapour pressures of the component liquids.

Dealing firstly with Type A; the molecular composition of the vapour from a binary liquid mixture is proportional to the partial pressures of the

component liquids multiplied by their concentrations in the mixture. In the case of two liquids whose partial pressures are indicated by QR and PS in Fig. 68 (A) it will be clear that the vapour will be richer than the liquid in the component of higher vapour pressure. It is therefore possible by distillation to separate the liquid mixture into fractions which are richer and poorer respectively in this more volatile component than the original liquid mixture. This process which is known as *fractional distillation* is of very great importance in the chemical industry. It is possible by such fractional distillation to isolate each of the component liquids of a mixture in the pure state.

So far it has been assumed that the liquid solution behaves in an ideal manner, but the same arguments however may be applied if the lines QR and PS in Fig. 68 (A) are not straight, but are curved indicating positive or negative deviation, so long as the total vapour pressure line—PR in Fig. 68 (A)—passes neither a through minimum nor a maximum.

If the molecular composition of the liquid and its vapour are plotted against the temperature of the boiling point a diagram such as that shown at Fig. 68 (B) is obtained. The upper curve represents the composition of the vapour whilst the lower curve represents the composition of the liquid. Thus, when at temperature T a liquid of composition L_1 commences to boil it gives rise to vapour of composition, V_1. Note that V_1 is richer than L_1 in the more volatile component liquid X. On distillation the residual liquid becomes progressively richer in the less volatile component liquid Y so that the boiling point of the liquid mixture rises steadily towards that of the less volatile component Y. If vapour V_1 is condensed it will produce liquid L_2 of the same composition, and if then liquid L_2 is heated vapour of composition V_2 will be produced which is much richer in component liquid X than initial liquid L_1. It is therefore possible by successive processes of vaporization and condensation to effect a separation of pure liquid X. In actual practice these processes are effected in one and the same operation by means of

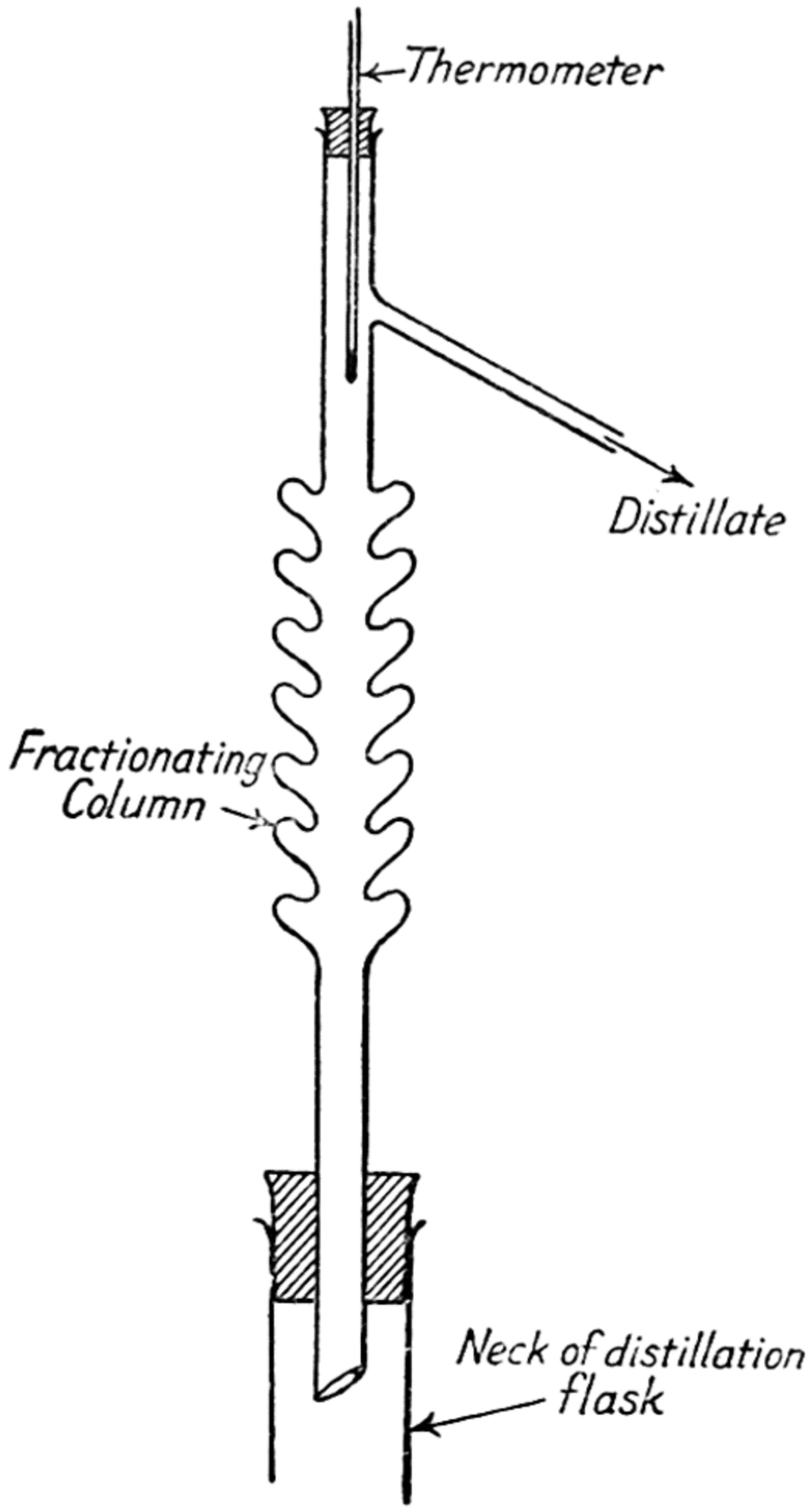


FIG. 69. Fractionating Column

a fractionating column (*see* Fig. 69). In the fractionating column the vapour passing upwards is gradually cooled so that it is progressively condensed, the condensing liquid being richer in the less volatile liquid *Y* than is the vapour, with the result that the proportion of liquid *X* in the vapour progressively increases until, under ideal conditions, the pure liquid *X* passes off from the top of the fractionating column.

Amongst other industrial processes the process of fractional distillation is employed for the separation of liquid oxygen from nitrogen in liquid air. In the case of binary liquid systems where the total vapour pressure curve exhibits a minimum as shown in Fig. 70 (*A*), it is impossible to separate

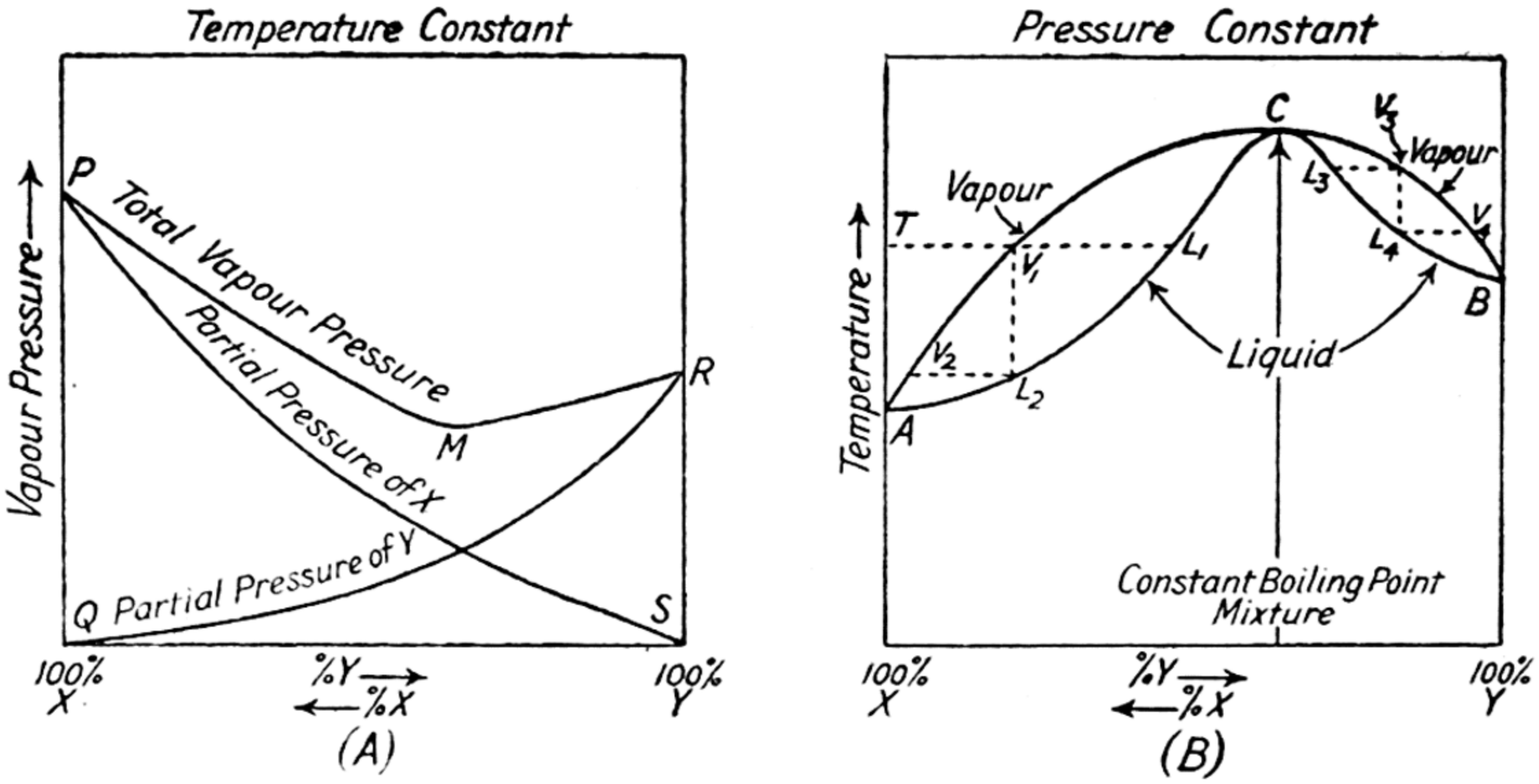


FIG. 70. Vapour Pressure—Composition and Temperature—Composition Curves with Minimum in Total Vapour Pressure Curve

the component liquids by distillation, as described above, into fractions consisting of pure *X* and pure *Y*. Instead, a fraction is obtained either of pure *X* or pure *Y*—according to the composition of the liquid mixture—along with a liquid mixture of constant boiling point having a composition corresponding to the maximum value on the curve *AB* (Fig. 70 (*B*)), that is the point *C*. This mixture of maximum boiling point corresponds to the minimum value of vapour pressure, the point *M* on the curve *PR* (Fig. 70 (*A*)). If liquid of composition L_1 is heated, it commences to boil at the temperature *T* evolving vapour of composition V_1; this vapour is richer in component liquid *X* than is the original liquid. When in the form of vapour V_1, it condenses to give liquid L_2 which, when heated, evolves vapour of composition V_2. Thus, the vapour becomes richer in component liquid *X* until finally the pure component *X* distils off. With progressive enrichment of the vapour in respect of liquid *X* there is a corresponding depletion in the residual liquid of component liquid *X* so that ultimately

this impoverishment in X causes the liquid contained within the distilling flask to attain the composition of the constant boiling-point mixture C (Fig. 70 (B)).

At the point C the liquid has the same composition as the vapour with which it is in equilibrium and consequently the two distil over together. Such mixtures which distil over unchanged are known as *azeotropic mixtures* or simply *azeotropes*. In a similar manner, it follows that a liquid of composition L_3 gives rise, on heating, to vapour V_3, which in turn cools to give liquid L_4, and this on heating evolves vapour V_4 and so on; so that in this case distillation will give rise to pure liquid Y in the first instance, but when the liquid remaining in the distilling flask attains the composition of the point C then the azeotropic mixture of this composition will distil over unchanged.

There are a number of common substances which form binary liquid mixtures giving rise to azeotropes. Some of the more important are enumerated below in Table 32.

TABLE 32

Maximum Boiling-point Mixtures
(*at* 760 *mm pressure*)

Mixture	Composition	Boiling Point
Hydriodic acid—Water . . .	58·00 per cent HI	127·00°C
Hydrobromic acid—Water . .	48·00 per cent HBr	125·00°C
Hydrochloric acid—Water . . .	20·22 per cent HCl	108·58°C
Hydrofluoric acid—Water . . .	37·00 per cent HF	120·00°C
Nitric acid—Water	68·00 per cent HNO_3	120·50°C
Sulphuric acid—Water . . .	98·70 per cent H_2SO_4	338·00°C

It should be noted that in the examples quoted in Table 32 all the pairs of liquids enumerated exhibit considerable affinity for one another and liberate heat, sometimes considerable, when mixed together.

In the case of the third class of binary liquid mixtures—those which exhibit a maximum on the total vapour pressure-composition curve—distillation gives the constant boiling-point mixture with the maximum vapour pressure, that corresponding to the point M on curve PR (Fig. 71 (A)), and the point C on the curve AB (Fig. 71 (B)). Thus, liquid of composition L_1 (Fig. 71 (B)) on heating evolves vapour of composition V_1 which cools to give liquid L_2. In turn L_2 on heating evolves vapour V_2 and so on until finally the azeotropic mixture C is attained. This mixture distils leaving the pure component liquid Y in the distilling flask. Some

TABLE 33

Minimum Boiling-point Mixtures

(*at* 760 *mm pressure*)

Mixture	Composition	Boiling Point
Ethyl alcohol—Water . . .	95·59 per cent C_2H_5OH	78·13°C
Ethyl alcohol—Ethyl acetate . .	46·40 per cent C_2H_5OH	71·80°C
Ethyl acetate—Water . . .	30·50 per cent water	70·40°C
Pyridine—Water	59·00 per cent C_5H_5N	92·00°C

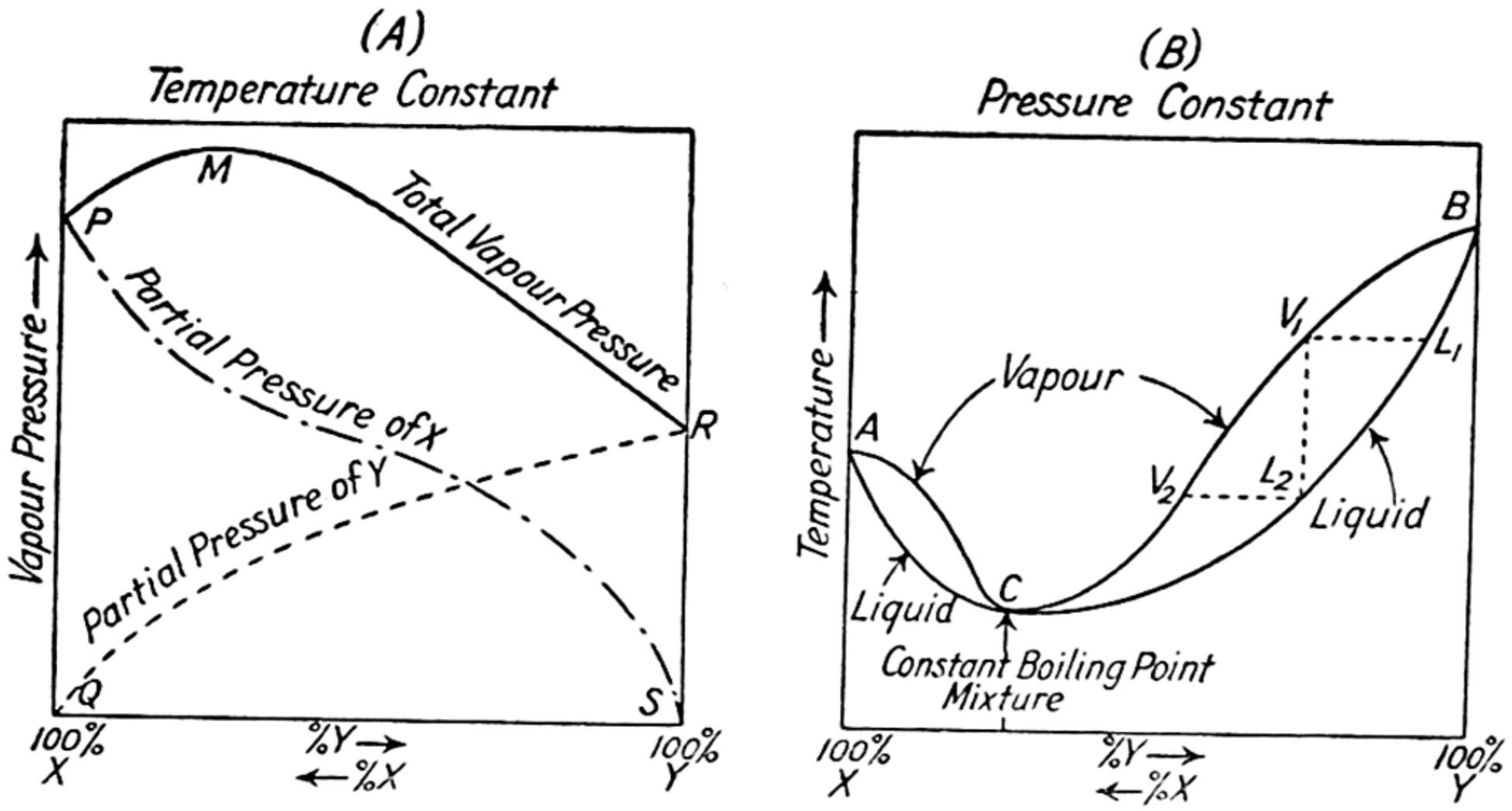


FIG. 71. Vapour Pressure—Composition and Temperature—Composition Curves with Maximum in Total Vapour Pressure Curve

examples of azeotropic mixtures of minimum boiling point are given in Table 33.

Two Liquids Partially Miscible in One Another. Not all liquids exhibit complete miscibility in one another. Thus, for example, if a little aniline or ether or phenol is added to water at atmospheric temperature the material will dissolve, but if further additions of the same solute are made a point will ultimately be reached when no further solution occurs and two liquid layers are formed. One of the layers is a saturated solution of the solute in water, and the other is a saturated solution of water in the organic compound constituting the solute in the first-named solution. There are thus two liquid solutions co-existent in equilibrium, such solutions are termed *conjugate solutions.*

If the vapour pressure of two liquids which are only partially soluble in one another is plotted against composition, a curve of the type shown in Fig. 72 will be obtained. This diagram which is for the water-ether system shows that water will hold up to about 7 per cent ether in solution after which, if more ether is added, an upper layer of ether saturated with water makes its appearance. Thus, the vapour pressure of the system remains at a constant value over a range of composition as indicated by the horizontal line QR, the addition of more ether merely altering the relative amounts of the two solutions. Ultimately, when sufficient ether has been added, there is then enough to dissolve the whole of the water present;

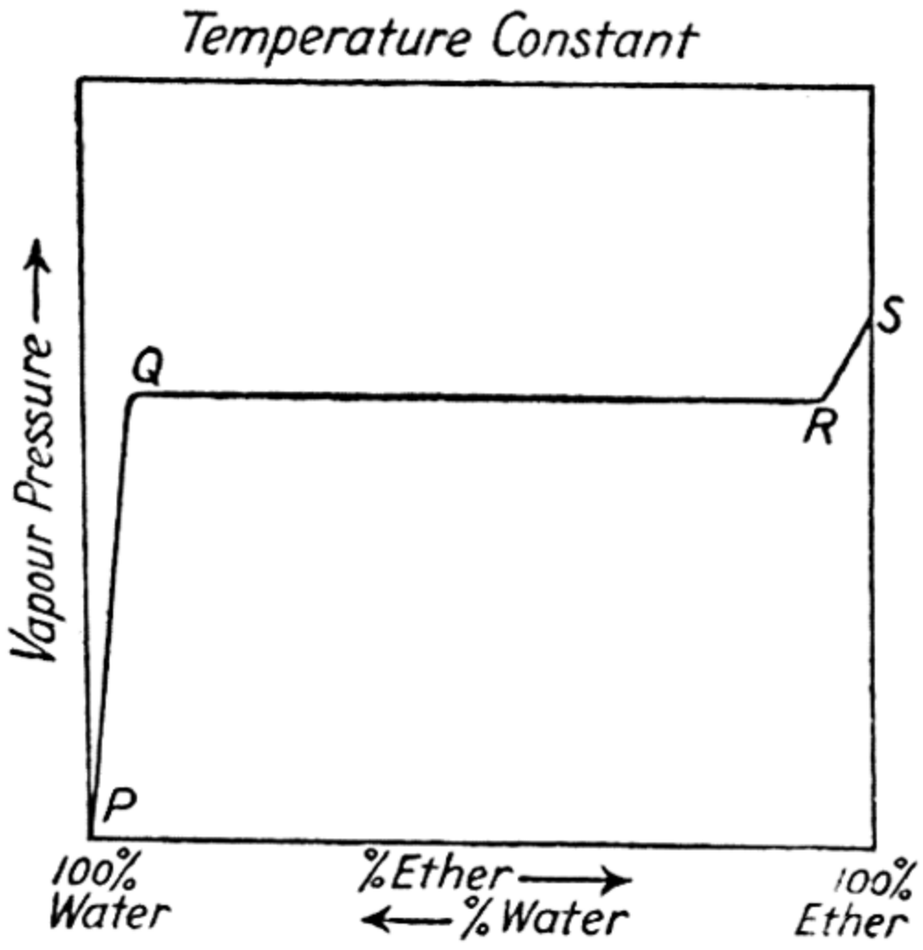


FIG. 72. Vapour Pressure—Composition Diagram for the System Water—Ether

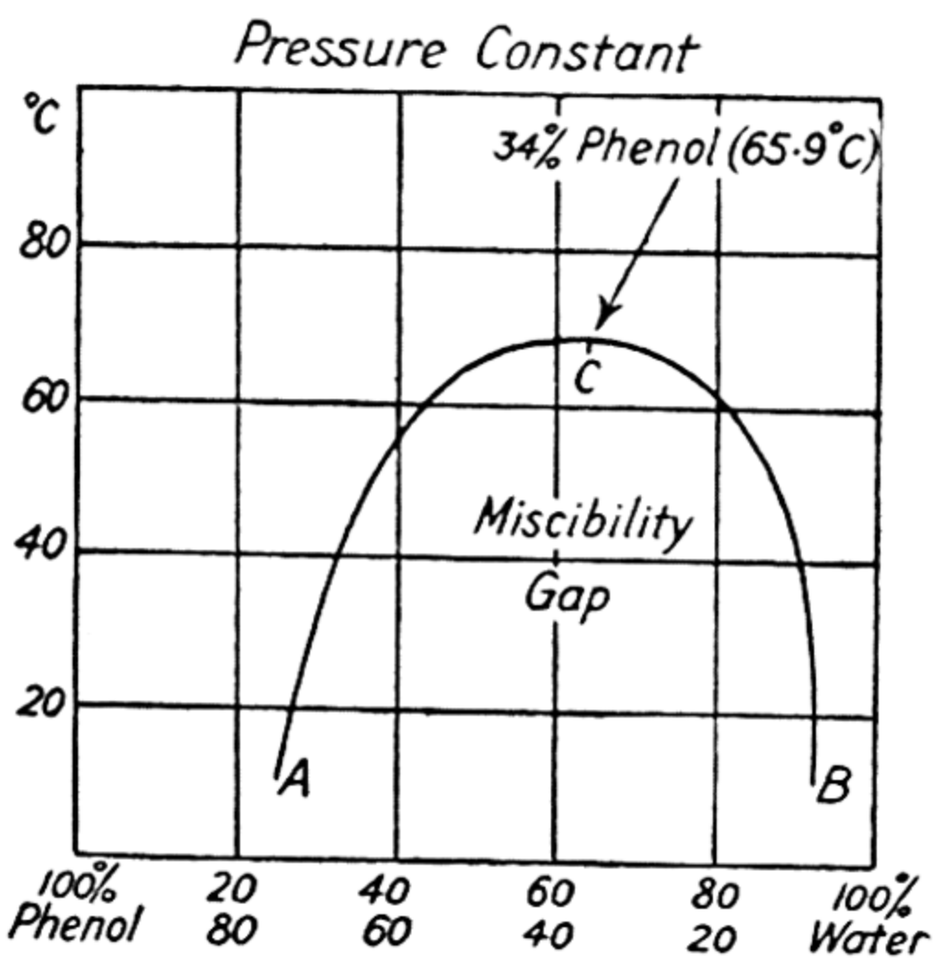


FIG. 73. Temperature—Composition Diagram for the System Phenol—Water

this is the state of affairs at the point R so that further additions of ether form an unsaturated solution of water in ether as indicated by the line RS and the vapour pressure of this solution progressively rises until the vapour pressure of pure ether is reached at the point S.

If the compositions of the conjugate solutions at different temperatures are plotted most systems will give a diagram of the type shown in Fig. 73, the diagram for the phenol-water system. From this diagram it will be noted that as the temperature rises the compositions of the two conjugate solutions approach one another until at the point C they become identical in composition. At all temperatures above the point C, and indeed at all points outside the curve ACB the two component substances phenol and water are freely miscible in one another in all proportions. The point C is known as the *critical solution temperature*.

The region enclosed by the curve ACB is usually referred to as the *miscibility gap*.

All mixtures outside the curve ACB consist of one liquid phase only; if

the vapour phase is neglected, and since there are two components, by the Phase Rule the number of degrees of freedom are

$$\begin{aligned} F &= C - P + 2 \\ &= 2 - 1 + 2 \\ &= 3 \end{aligned}$$

Since the pressure variable, however, is taken as fixed at one atmosphere, the number of degrees of freedom will be 2; these are temperature and concentration and both these must be stated to define completely a system consisting of only one phase.

In the case of certain binary systems (e.g. triethylamine-water system) the solubilities of the two components decrease with rising temperature; thus, as the temperature is progressively lowered the mutual solubilities of the two components increase until a certain critical temperature is finally reached below which the two liquid solutions are miscible in all proportions. Not many systems of this type have been investigated in detail over a wide temperature range, but in the case of those systems which have been thus examined it is found that the mutual solubility of the components does not continue to decrease indefinitely if the temperature is raised sufficiently, but ultimately the system commences to behave in the normal manner as typified by the phenol-water system (*see* Fig. 73), that is, the mutual solubilities of the components increase with rising temperature until ultimately the two solubility curves join, as in the phenol-water system. In the case of such systems, therefore, the solubility curve consists of a closed curve, all points outside of which represent a homogeneous liquid solution of the two component substances, whilst within the curve exist the two conjugate solutions as two separate layers. One of the best known examples of such a system is that of nicotine and water. The diagram for this system is shown in Fig. 74.

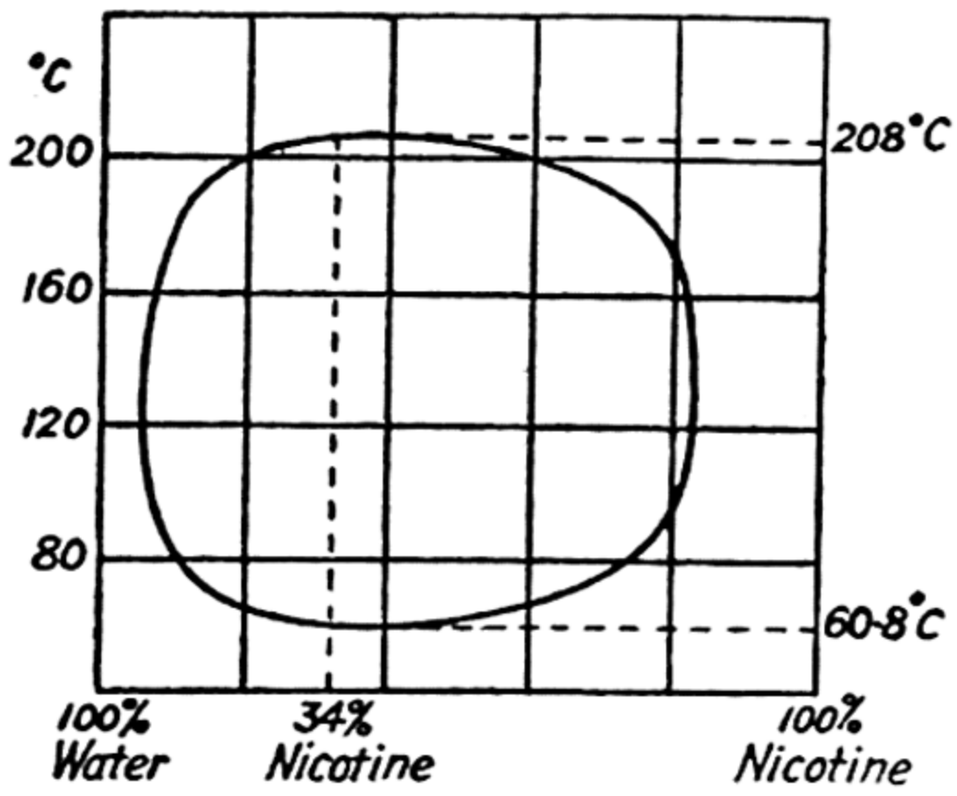


FIG. 74. Temperature—Composition Diagram for the System Water—Nicotine

Two Liquids which are Immiscible in One Another. When two immiscible liquids are placed together in the same vessel they separate out into two separate and quite distinct layers. When this mixture is heated, each of the liquids exerts its own vapour pressure peculiar to the temperature involved. As the temperature is raised the vapour pressure of the mixture gradually rises until it attains that of the atmosphere and the system boils. It is to be noted here that at the boiling point of a system of two immiscible liquids, the sum of the vapour pressures of the two liquids is equal to the

atmospheric pressure and therefore the vapour pressure of any single liquid is less than the atmospheric pressure and the temperature at which boiling occurs is lower than the boiling point of the more volatile liquid present. For example, for the system water-nitrobenzene which at 760 mm pressure boils at 99°C, the relevant data are—

	Boiling Point	*Vapour Pressure* at 99°C
Water	100°C	733 mm
Nitrobenzene	211°C	27 mm

Distillation in Steam. Suppose that two immiscible liquids have vapour pressures P_1 and P_2 at the boiling point of the liquid mixture, and that their respective molecular weights are M_1 and M_2. The relative weights of these two liquids found in the vapour evolved from the mixture will therefore be n_1M_1 and n_2M_2 respectively where n_1 and n_2 are the number of molecules of each substance in the vapour. Since the ratio n_1/n_2 is equal to the ratio P_1/P_2, it follows that—

$$\frac{\text{Weight of } M_1 \text{ in distillate}}{\text{Weight of } M_2 \text{ in distillate}} = \frac{P_1M_1}{P_2M_2} \quad . \quad . \quad . \quad (8)$$

These facts are utilized in the process of "steam distillation" whereby a substance more or less immiscible with water and possessing a higher boiling point than water can be distilled at a much lower temperature by bubbling steam through it. Under these conditions the mixture boils freely, that is, it distils, when the combined vapour pressure of the two component liquids equals that of the atmosphere. Thus a mixture of water and chlorobenzene distils at a temperature of 90·3°C when the atmospheric pressure is 740·2 mm, the vapour pressure of the two constituents being 530·1 mm and 210·1 mm respectively at this temperature. Therefore, from equation (8)

$$\frac{\text{Weight of chlorobenzene in distillate}}{\text{Weight of water in distillate}} = \frac{112{\cdot}5 \times 210{\cdot}1}{18 \times 530{\cdot}1}$$
$$= 2{\cdot}48$$

The distillate should therefore contain 71·2 per cent of chlorobenzene by weight; in actual fact, a typical experimental value is 71·4 per cent so that the agreement is very good indeed. It should be noted that chlorobenzene has a boiling point of 132°C, but by steam distillation it is possible to distil it 42°C lower, and the distillate contains over 70 per cent of chlorobenzene.

The Distribution Law (or Partition Law). The distribution law may be expressed thus—if to a system of two phases made up of two immiscible, or only slightly miscible, components existing as two distinct liquid layers, there is added a third substance soluble in both layers, then the added

substance will distribute itself between the two phases in such a way that the ratio of its concentrations in each phase is constant and independent of the amount of added substance provided that this substance exists in the same type of molecular species in each phase.

The Distribution Law may be expressed mathematically as follows—

$$\frac{\text{Concentration of solute } X \text{ in solvent } A}{\text{Concentration of solute } X \text{ in solvent } B} = K \quad . \quad . \quad (9)$$

where K = distribution coefficient (or partition coefficient).

This law is of very wide application; for example, as mentioned on p. 169, Henry's Law for the influence of pressure on the solubility of a gas may be regarded as one form of the distribution law in which the gas may be considered as distributing itself, in a constant ratio, between free space and the solvent. Thus, as given on p. 169, the mathematical expression of Henry's law (Eq. (7)) is as follows—

$$\frac{\text{Concentration of gas in gaseous layer}}{\text{Concentration of gas in solution}} = K$$

The similarity of equations (7) and (9) should be noted. Some examples of the behaviour of solutes illustrating the distribution law are given in Table 34.

TABLE 34

Distribution Coefficients

(*Concentrations in moles/litre*)

Iodine between Carbon Tetrachloride (I) and Water (II)		Mercuric Chloride between Water (I) and Benzene (II)	
c_I	c_I/c_{II}	c_I	c_I/c_{II}
0·02	85·1	0·001	11·97
0·04	85·2	0·005	12·31
0·06	85·4	0·010	12·73
0·08	86·0	0·015	13·16
0·10	87·5	0·025	14·01

As stated above, the distribution coefficient is only constant when the solute exists in the same type of molecular species in both solvents; if this is not the case the numerical value of the distribution coefficient will vary with variation in the concentration of the solution. This is exemplified by the distribution of acetic acid between carbon tetrachloride and water as quoted in Table 35.

TABLE 35

Distribution of Acetic Acid between Carbon Tetrachloride and Water

Concentration in CCl_4	Concentration in Water	Distribution Coefficient	
c_1	c_{II}	c_I/c_{II}	$\sqrt{c_I}/c_{II}$
0·0096	0·684	0·0140	0·143
0·0187	1·021	0·0183	0·132
0·0460	1·691	0·0266	0·127

From this table it will be noted that the ratio c_1/c_{11} is not constant, but increases as the concentration rises. From previous discussion (*see* p. 158) it will be recalled that although acetic acid has a normal molecular weight in aqueous solution, it has twice the normal molecular weight in carbon tetrachloride. In this latter solvent, therefore, the following equilibrium will exist.

$$\underset{(1-\alpha)c}{(CH_3COOH)_2} \rightleftharpoons \underset{2\alpha c}{2CH_3COOH}$$

If the initial concentration of double molecules is c, and if a fraction α is dissociated into single molecules, then on the application of the law of mass action (*see* p. 219)—

$$K = \frac{(2\alpha c)^2}{(1-\alpha)c}$$

$$= \frac{4\alpha^2 c^2}{(1-\alpha)c}$$

$$= \frac{4\alpha^2 c}{(1-\alpha)}$$

therefore,

$$\alpha^2 = \frac{K(1-\alpha)}{4c} \quad . \quad . \quad . \quad . \quad (10)$$

If the numerical value of α is small, then $(1-\alpha)$ may be taken as unity, thus equation (10) is capable of simplification—

$$\alpha^2 = \frac{K}{4c} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

so that α varies as $1/\sqrt{c}$, and in the specific case of acetic acid distributed between carbon tetrachloride and water,

$$\alpha c = \text{Constant} \times c \times 1/\sqrt{c}$$

$$= \text{Constant} \times \sqrt{c} \quad . \quad . \quad . \quad . \quad (12)$$

If the concentration in carbon tetrachloride is denoted by c_I, and the concentration in water by c_{II} the distribution coefficient, $\sqrt{c_I}/c_{II}$ should be constant; Table 35 shows that within close limits this is the case.

From the above discussion it will be clear that the study of the distribution of a solute between two solvents is of value in determining whether or not the solute is either associated or dissociated in a particular solvent, and also as a means of determining to what degree such a change has occurred.

Extraction of a Solute with a Second Solvent. The widely-employed process of extraction with ether and similar solvents is dependent upon the distribution of a solute between two partially miscible or immiscible liquids. In this process a solution of the solute in question is shaken up with a second solvent, in which the solute is more soluble. The solute then distributes itself between the two solvents, forming solutions which are capable of ready separation. This process is widely used as a means of extracting organic substances from aqueous solution. Since the solubility of such substances is usually greater in organic solvents than in water it is common practice to employ organic solvents for the second solvent. Also, since the solubility of organic compounds is lower in aqueous solutions of electrolytes than in pure water, electrolytes are commonly added to the water layer to facilitate still further the extraction process. In other words, the organic solute tends to be "salted out" from its aqueous solution. The efficiency of extraction under a given set of conditions may be calculated as follows—

Let a ml of a solution (Phase I) containing c g of a dissolved solute be extracted repeatedly with b ml of a second solvent (Phase II).

If after the first extraction the weight of solute remaining in Phase I is c_1 g, then the concentration per millilitre in Phase I will be c_1/a, whilst that in Phase II is $(c - c_1)/b$. Thus, by application of the Distribution Law—

$$\frac{c_1/a}{(c - c_1)/b} = K \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Therefore,
$$c_1 = c\,\frac{Ka}{Ka + b} \quad . \quad . \quad . \quad . \quad (14)$$

If, after a second extraction, c_2 g of the solute remain dissolved in Phase I, then—

$$c_2 = c_1\,\frac{Ka}{Ka + b} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$= c\left(\frac{Ka}{Ka + b}\right)^2 \quad . \quad . \quad . \quad . \quad (16)$$

Equation (16) is capable of generalization, so that after the nth extraction, the weight, c_n g of solute remaining in Phase I is—

$$c_n = c\left(\frac{Ka}{Ka + b}\right)^n \quad . \quad . \quad . \quad . \quad (17)$$

In practice it is more efficient to use a number of small portions of the extracting solvent in a number of individual extractions, rather than use the whole of this solvent in a single extraction. This may be illustrated by considering the extraction of benzoic acid from its aqueous solution by means of ether. The distribution coefficient for this acid distributed respectively between water and ether is 0·0125.

Suppose, for example, that the weight of benzoic acid initially present in the aqueous solution to be 20 g and the volume of this solution is 1000 ml, and the volume of the ether used for the extraction is 600 ml. Then, if only a single extraction is practised, on introduction of these data in equation (17)—

$$c_n = 20\left(\frac{0{\cdot}0125 \times 1000}{(0{\cdot}0125 \times 1000) + 600}\right)$$

= 0·408 g of benzoic acid remaining in the aqueous solution.

On the other hand, if the benzoic acid is extracted with three separate portions of ether, each of 200 ml (the same total volume of ether being used as in the previous case), then—

$$c_n = 20\left(\frac{0{\cdot}0125 \times 1000}{(0{\cdot}0125 \times 1000) + 200}\right)^3$$

= 0·00407 g of benzoic acid will remain in the aqueous solution, and the extraction may therefore be said for all practical purposes to be "complete."

Obviously complete extraction is impossible in practice since although the quantity, $\left(\frac{Ka}{Ka + b}\right)^n$ in equation (17) becomes progressively smaller as the number of extractions increases, it never actually becomes zero.

SOLUTIONS OF SOLIDS IN LIQUIDS

In the case of binary systems, the complete graphical representation of the three conditions of freedom—temperature, pressure and concentration as postulated by the phase rule—renders necessary the employment of three-dimensional models. For many purposes, however, simplification of graphical representation is desirable, and this is attained by modification of the statement of the phase rule. In other words, one of the variables is fixed arbitrarily. For solid—liquid systems it is most convenient to fix the pressure variable since such systems are almost always studied in vessels open to

the atmosphere, that is the pressure is fixed at one atmosphere. The modified phase rule thus becomes—

$$F = C - P + 1 \quad . \quad . \quad . \quad . \quad (18)$$

In this way the graphical interpretation of solid—liquid equilibria is effected by the use of ordinary rectangular co-ordinates representing the two variables, temperature and concentration respectively. Some of the most common, and also the most important solid—liquid systems, are those of metallic alloys, and in the discussion which follows, frequent reference will therefore be made to such systems.

Solid—liquid systems may be classified as follows—

1. Systems in which the two components are completely soluble in one another in the liquid state but are—

(*a*) completely insoluble in one another in the solid state, or
(*b*) partially soluble in one another in the solid state, or
(*c*) completely soluble in one another in the solid state.

2. Systems in which the two components are partially soluble in one another in the liquid state, but are—

(*a*) completely insoluble in one another in the solid state, or
(*b*) partially soluble in one another in the solid state.

Type 1 (*a*) Systems. If a vessel such as a crucible containing a small quantity of a pure molten metal is allowed to cool slowly so that freezing ultimately occurs, the relationship between the temperature of the metal and time may be represented by means of a cooling curve, the general form of which is shown in Fig. 75, curve *A*. The freezing point of the pure metal is the temperature of the horizontal portion *bc* of this curve, being due to the liberation of the latent heat of fusion of the metal. Thus, in this curve, the portion *ab* represents the cooling of the molten metal, the horizontal portion, *bc*, the freezing process, and the portion, *cd*, the cooling of the solidified metal. It should be noted that the portion *cd* exhibits a steeper slope than the portion *ab* since the specific heat of the solidified metal is less than that of the liquid metal.

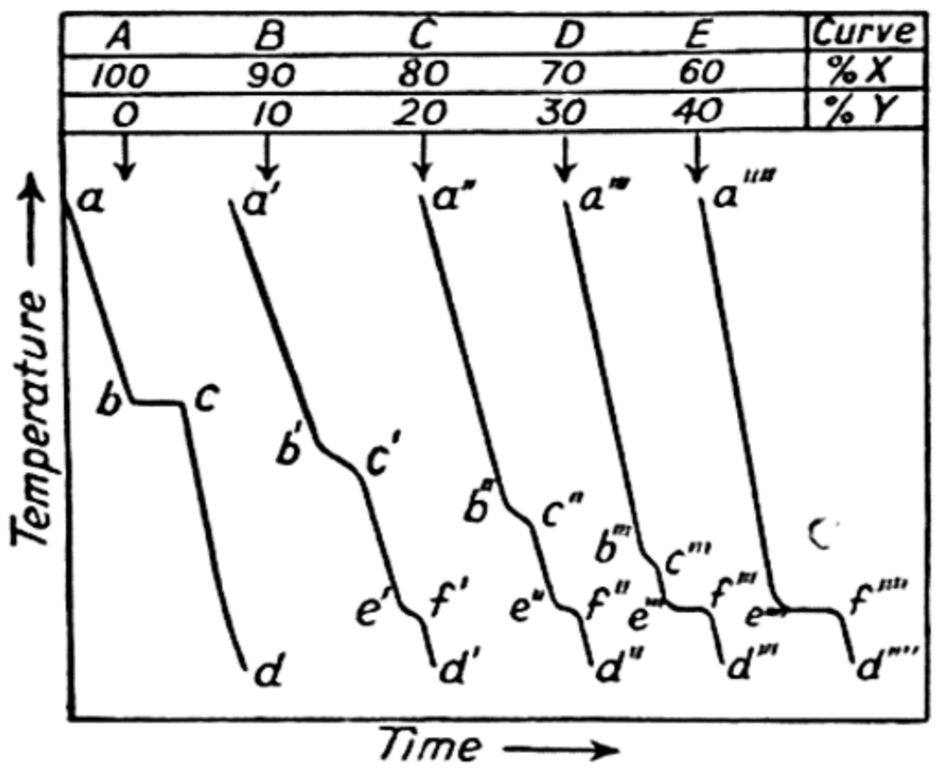


FIG. 75. Cooling Curves for a Series of Alloys

In the foregoing discussion only one component of a system was involved, but, if the second component of a binary system is present, and—still confining attention to metallic systems—if an alloy of two metals is formed, the freezing process is different.

Consider an alloy of two metals X and Y containing 90 per cent of the former metal and 10 per cent of the latter. If the cooling curve for this alloy is determined it will be found to be similar in type to that shown as curve B (Fig. 75), in which the freezing of the pure metal X commences at the point b'. It should be noted that the temperature of the point b' is lower than that of b in curve A. Now if other alloys are prepared containing progressively greater concentrations of the pure metal Y it will be found that the freezing of the pure metal X commences at progressively lower temperatures as indicated by the points, b'' and b''' of the curves C and D

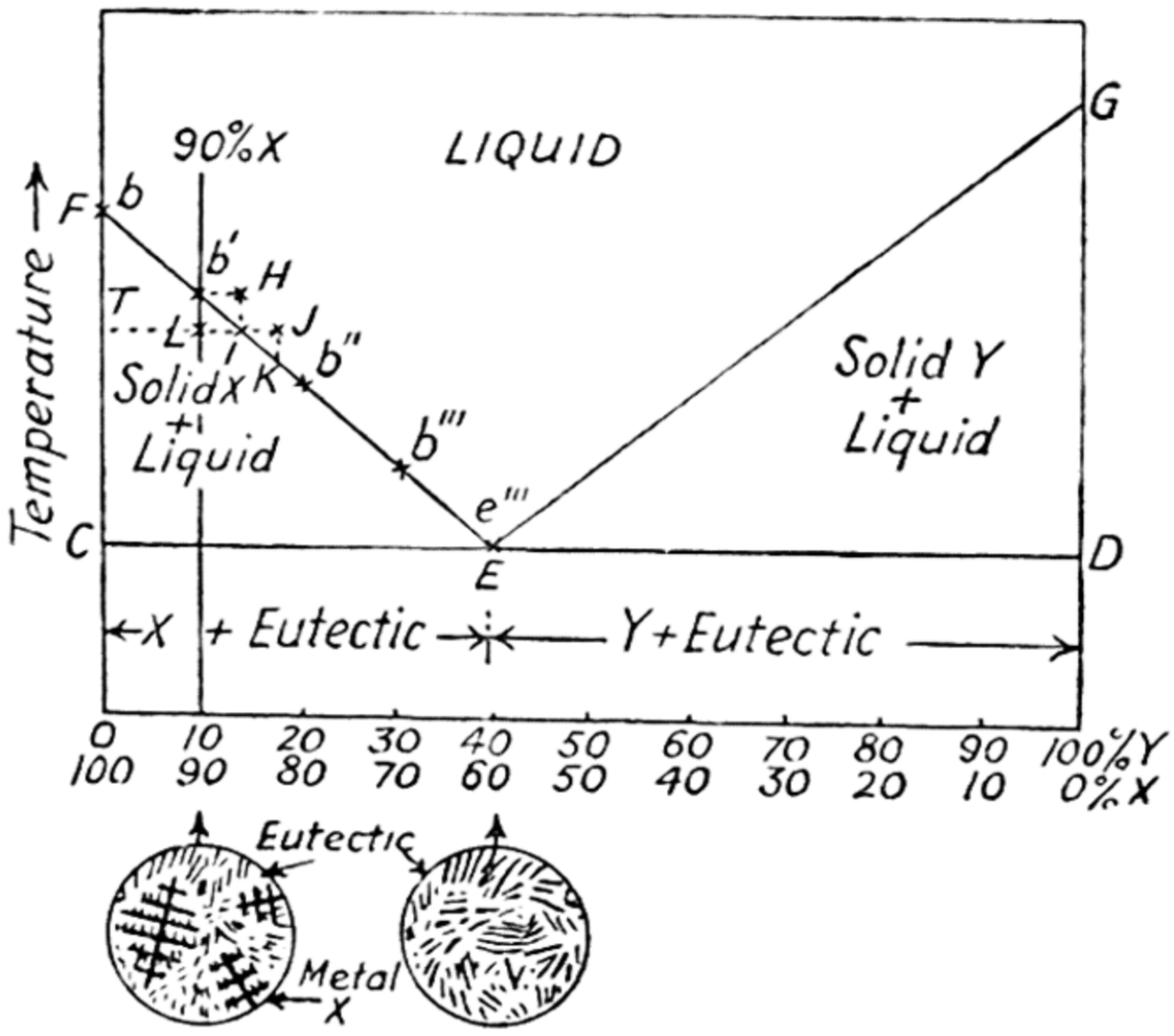


FIG. 76. Equilibrium Diagram for Two Substances, X and Y Completely Soluble in one another in the Liquid State, and Completely Insoluble in one another in the Solid State

(Fig. 75). The sum of these results may be represented on one diagram (Fig. 76) in which the line FE represents the progressive lowering of the freezing point of the pure metal X by the addition of the pure metal Y; in this diagram it should be noted that the horizontal axis represents the composition of the alloy.

In a similar manner, the addition of pure metal X to the pure metal Y gives rise to a progressive lowering of the freezing point of the latter metal; this general process is represented by the line GE (Fig. 76). The lines FE and GE intersect at the point E, which represents the composition of an alloy possessing the lowest freezing point of the whole series; this particular alloy is known as the *eutectic alloy*, or more usually, simply as the *eutectic*. No solid material occurs at temperatures above those of the line, FEG which is termed the *liquidus*.

Reverting to curve B (Fig. 75) it will be observed that the portion $b'c'$ is no longer horizontal as was the portion bc in curve A; in other words, the

solidification of the alloy does not occur at a constant temperature as it does in the case of a pure metal, but over a range of temperature. This is due to the fact that in the case of the alloy containing 10 per cent of metal *Y*, the first crystal of metal is formed at the temperature of the point *b′* (*see* Fig. 76) and this gives rise to an enrichment of the residual molten alloy in metal *Y*; in other words the composition of the molten alloy changes, say to the composition represented by the point *H*. It should be clearly noted that the actual change in composition is very small indeed, the large change in liquid composition being used here only to make the freezing process more clear. Now liquid of composition *H* may persist in the liquid state until the temperature of the point *I* is reached, when a further amount of pure metal *X* crystallizes out. This gives rise to yet a further change in the composition of residual liquid alloy, say, to the point *J*. It is this gradual process which gives rise to the sloping portion, *b′c′* of the curve *B* (Fig. 75). With alloys containing yet greater contents of metal *Y* this region of the cooling curve becomes progressively steeper as indicated by the portions, *b″c″* and *b‴c‴* of the curves *C* and *D* respectively.

Reverting again to curve *B* (Fig. 75), as more and more pure metal *X* crystallizes out, the composition of the residual liquid alloy changes slowly down the branch of the liquidus *FE* until ultimately the eutectic composition is attained. At the eutectic, the two metals *X* and *Y* crystallize simultaneously until all the liquid alloy has changed to a mixture of solid *X* and solid *Y*, this process taking place at constant temperature; when all the homogeneous liquid alloy is transformed to a mixture of two solid metals the temperature commences to fall again. From a consideration of Fig. 75 it will be noted that the cooling curves for all the alloys of the metals *X* and *Y* exhibit a common arrest at the temperature of the eutectic, that is, the identical temperature of the portions *e′f′*, *e″f″*, *e‴f‴* and *e⁗f⁗* of the curves *B*, *C*, *D* and *E* respectively. It is therefore possible to draw a horizontal line, parallel to the composition axis, through the eutectic point; this is the line *CED* (Fig. 76). Below the temperature of the line *CED* the alloys are completely solid and the name *solidus* is therefore given to *CED*.

At all temperatures below the solidus the alloy containing 90 per cent *X* and 10 per cent *Y* consists of primary crystals of the pure metal *X* surrounded by the eutectic mixture composed of crystals of the two metals *X* and *Y*; this structure which may be observed in specimens after polishing and suitable etching is shown diagrammatically in Fig. 76. As the content of metal *Y* increases, so in the solid condition the microstructure of alloys shows less of the pure metal *X* and more of the eutectic until, in the case of an alloy containing 40 per cent *Y*, the microstructure is composed entirely of the eutectic mixture of the two metals *X* and *Y*; this is also shown diagrammatically in Fig. 76.

Above the liquidus *FEG* (Fig. 76) there exists only one phase, the

homogeneous liquid solution of the two component metals X and Y, therefore applying the modified phase rule—

$$\begin{aligned} F &= C - P + 1 \qquad . \qquad . \qquad . \qquad . \quad (18) \\ &= 2 - 1 + 1 \\ &= 3 \end{aligned}$$

There are thus two degrees of freedom; in other words, temperature and concentration can be varied independently. Such a system is said to be *bivariant*.

When the temperature falls, however, so that the liquidus is reached, say at the point b', then there are two phases present, namely liquid alloy of composition b', and the solid metal X. Therefore—

$$\begin{aligned} F &= 2 - 2 + 1 \\ &= 1 \end{aligned}$$

from which it follows that it is impossible to have solid metal X and liquid alloy of composition b' at any temperature other than that of the point b'; in other words, a change in temperature causes a corresponding change in the composition of the liquid alloy in equilibrium with the solid metal X. Alternatively, a change in composition of the liquid alloy must be accompanied by a corresponding temperature change. Thus, the fixing of either the temperature variable or the composition variable immediately fixes the other variable. Such a system having only one degree of freedom is said to be *univariant*.

At the eutectic point itself there are three phases present, namely, solid metal X, solid metal Y, and the liquid alloy of eutectic composition. Thus—

$$\begin{aligned} F &= 2 - 3 + 1 \\ &= 0 \end{aligned}$$

and, since it possesses no degrees of freedom, this system in equilibrium is said to be *invariant*. In other words, it is only possible to have present at one and the same time these three phases at one specific temperature and one liquid composition.

Compound Formation. In systems of the type discussed above the two components are incapable of reaction with one another, but such is not always the case, and in metallic systems particularly, compound formation is of frequent occurrence. The existence of a compound is often indicated by either the presence of a maximum, or the presence of a discontinuity on the liquidus curve. Thus, in the case of the system for which the equilibrium diagram is shown in Fig. 77, a compound, designated $X_m Y_n$ is formed by the two component substances X and Y, the composition of this compound being indicated by a maximum on the liquidus curve.

Examination of this diagram shows that it may be regarded as being composed of two simple systems, $X - X_m Y_n$ and $Y - X_m Y_n$, so that the cooling of all melts is similar in type to that described for the alloy containing 90 per cent X in Fig. 76.

In Fig. 77 the compound $X_m Y_n$ is said to have a *congruent melting point* since both the liquid solution and the solid of this composition are capable of co-existence at the melting point of the compound; in other

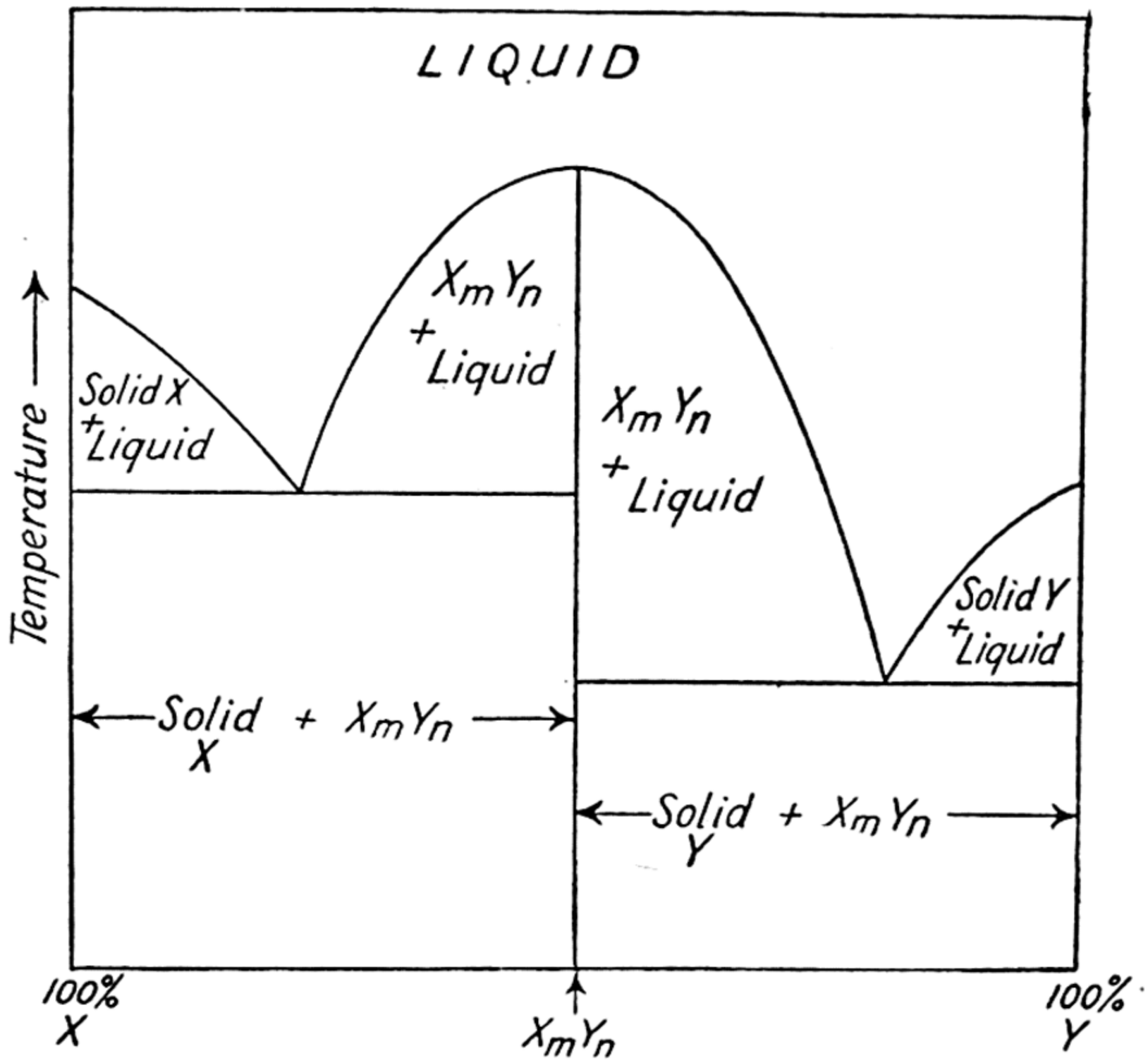


FIG. 77. Equilibrium Diagram for a Binary System in which a Compound is Formed with a Congruent Melting Point

words, the compound $X_m Y_n$ is said to be a *stable compound.* The two components of some binary systems often form more than one compound as exemplified by the system CaO-Al_2O_3 as shown in Fig. 78. This system is of great technological importance in the refractory and the ceramic industries.

Fig. 79 shows a system in which a compound occurs whose existence is indicated by a discontinuity on the liquidus curve at the point A. In this case the compound decomposes below its theoretical melting point at the temperature of the point B. The point A is known as a *peritectic point.* In the case of melts having compositions between the points A and D at the temperature of the line AD there are in equilibrium

$$X_m Y_n \rightleftharpoons Y + (\text{Liquid solution of } X \text{ in } Y)$$

Thus, there are present three phases, and by the arguments of the Phase Rule the system is invariant. Temperature and composition must therefore remain fixed until one of the phases disappears; if cooling is taking

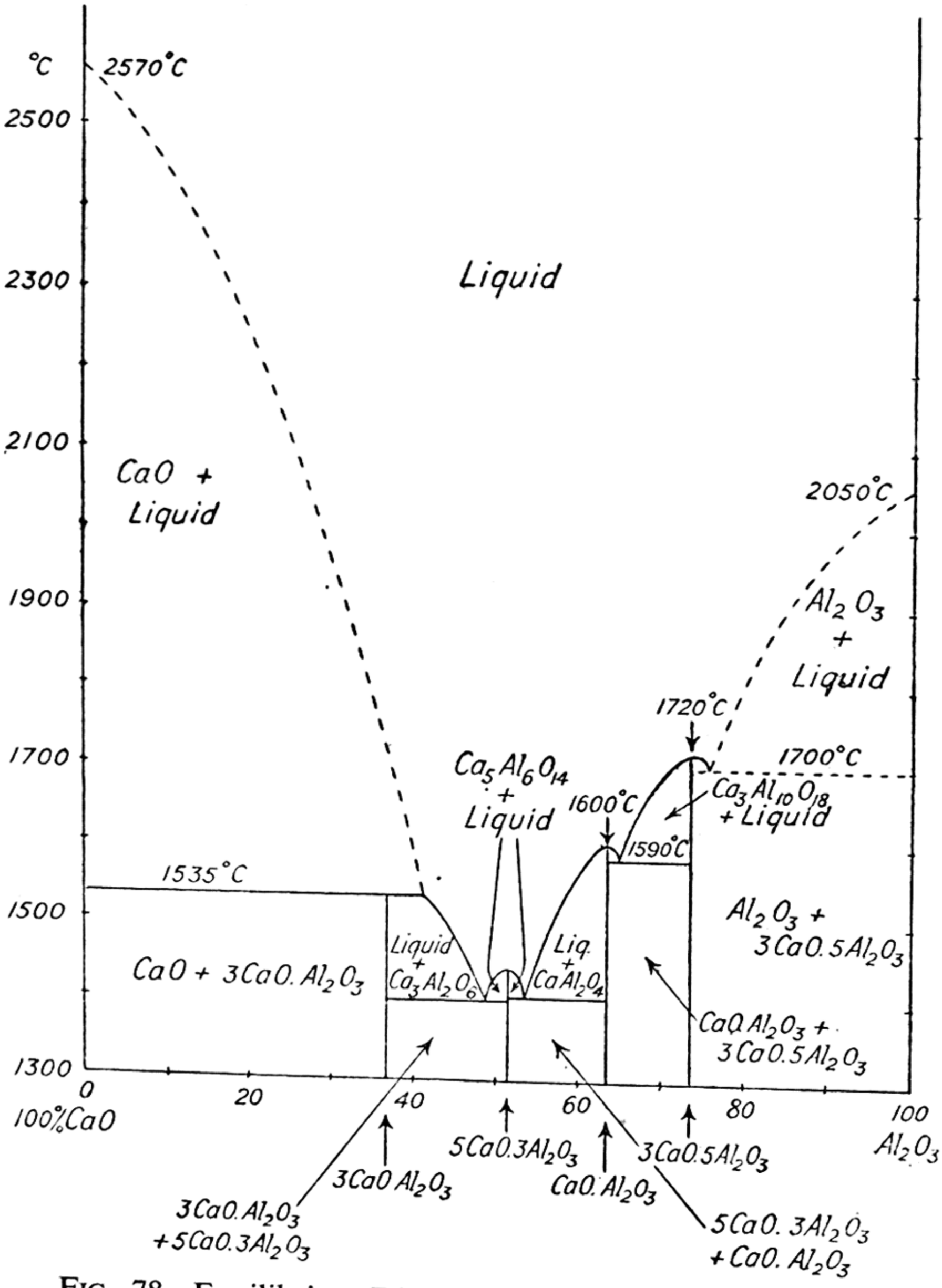


FIG. 78. Equilibrium Diagram for the System CaO-Al_2O_3

place, it is the liquid phase which disappears; if heating occurs, it is the compound $X_m Y_n$ which disappears. Compounds of the type $X_m Y_n$ in this diagram (Fig. 79) are often said to have *incongruent melting points* since solid of this composition is incapable of co-existence with the liquid

solution. The formation of such an unstable compound is typified by the system SiO_2-Al_2O_3, as shown in Fig. 80.

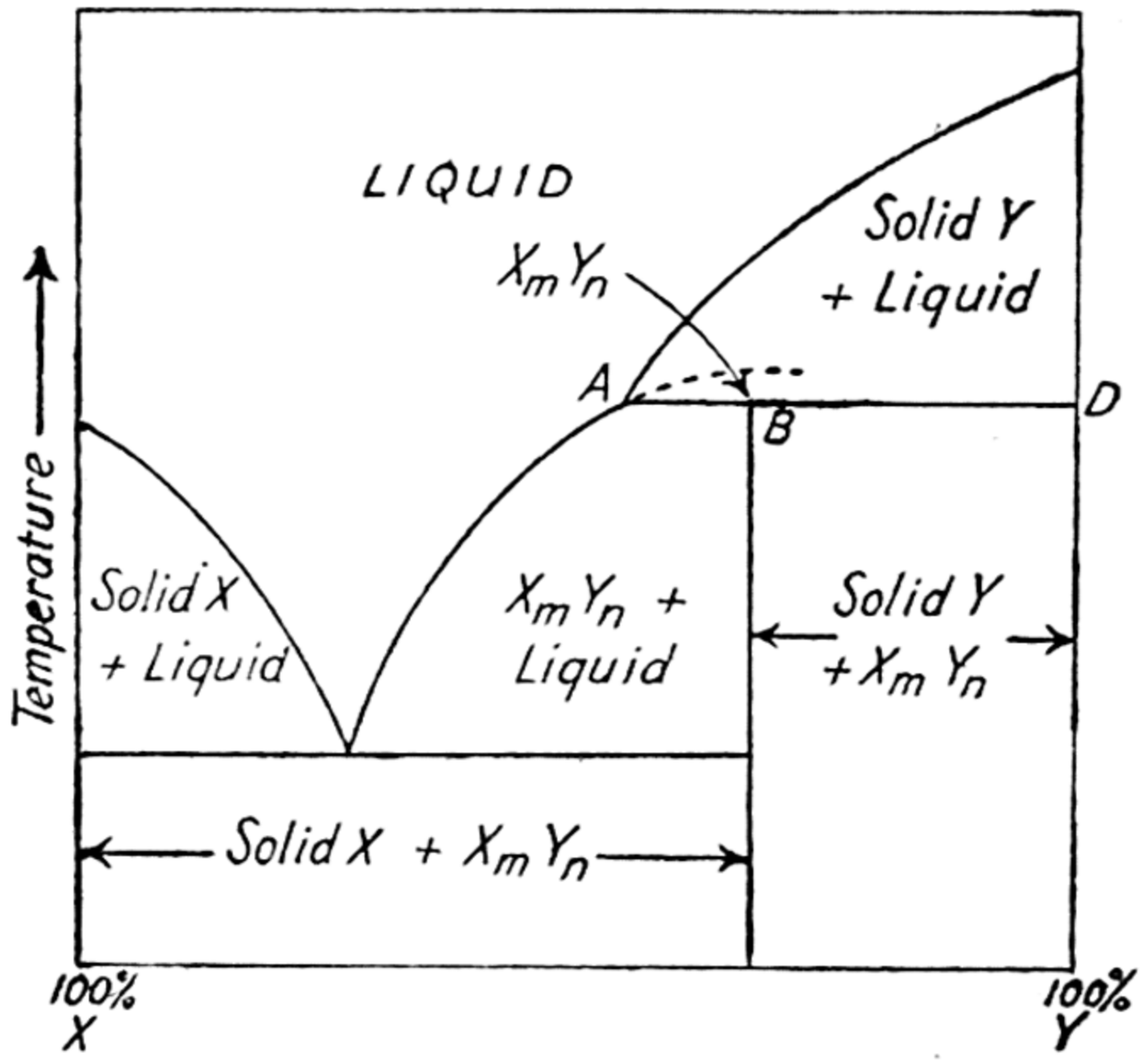


FIG. 79. Equilibrium Diagram for a Binary System in which a Compound is formed with an Incongruent Melting Point

Salt-Water Systems. Binary systems involving a salt and water are, in general, of similar types to those described in the foregoing discussion.

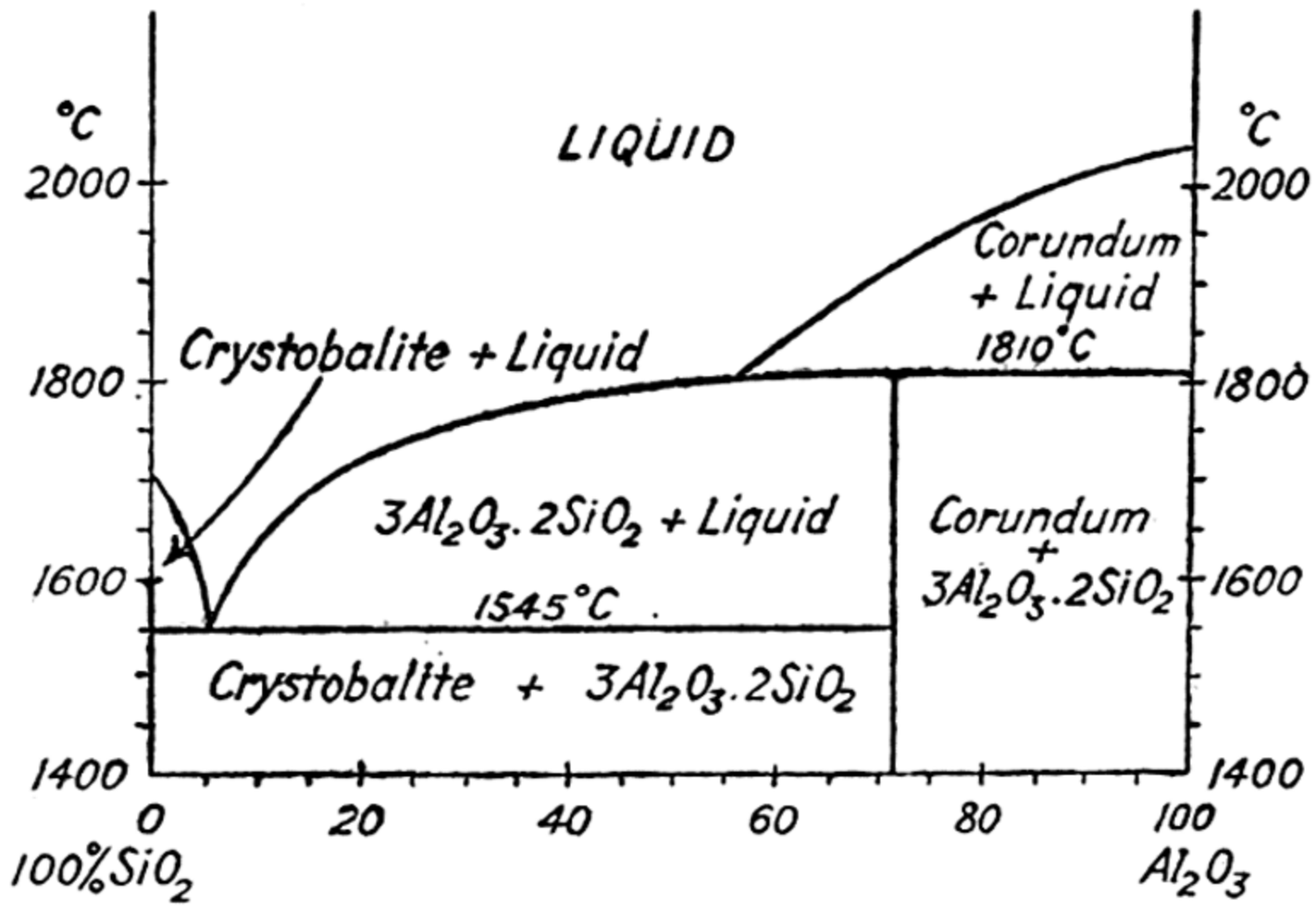


FIG. 80. Equilibrium Diagram for the System SiO_2-Al_2O_3

Thus, for example, Fig. 81 depicting the system ammonium sulphate-water is similar to Fig. 76, whilst Fig. 82 is similar to Fig. 80, and in addition the systems NaOH-water and $Mn(NO_3)_2$-water are similar in type to Fig. 77.

An examination of equilibrium diagrams for salt-water systems provides the explanation for the mechanism by which freezing mixtures are opera-

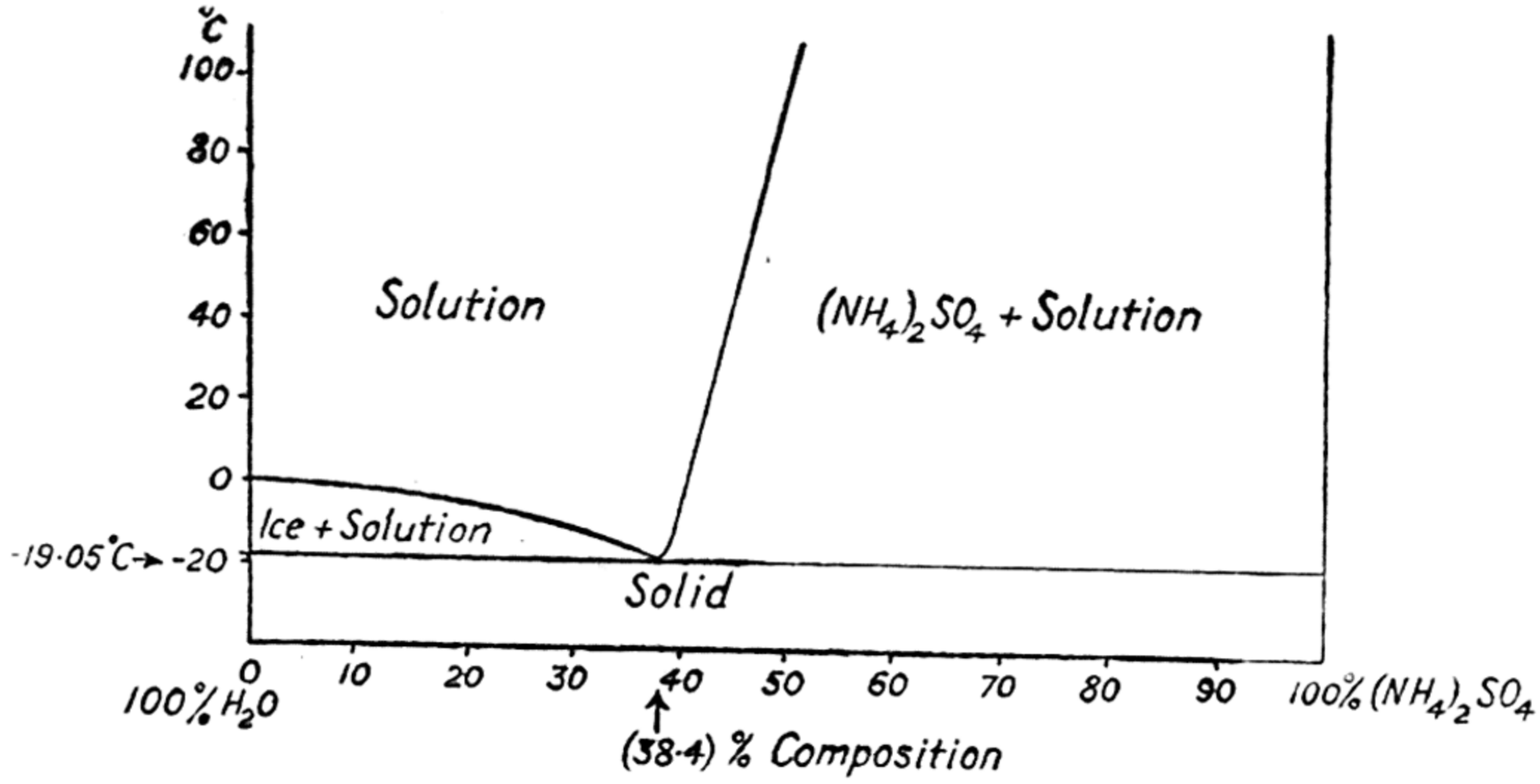


FIG. 81. Equilibrium Diagram for the System $(NH_4)_2SO_4$-Water

tive. Referring to Fig. 81, it will be noted that when ammonium sulphate is added to a mixture of ice with a little water at 0°C, some of the ammonium sulphate will dissolve forming an aqueous solution of this salt; there will

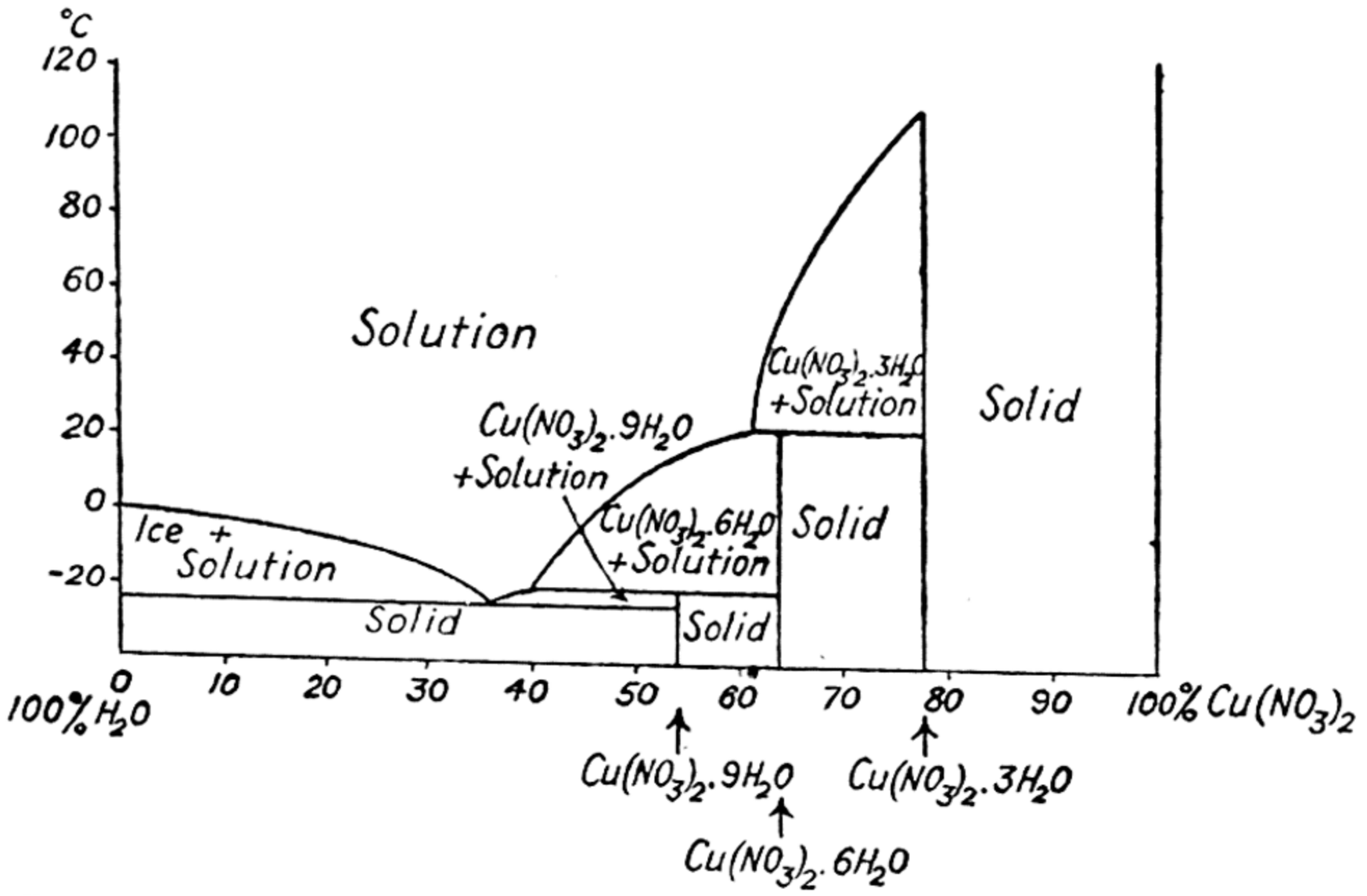


FIG. 82. Equilibrium Diagram for the System $Cu(NO_3)_2$-Water

thus be present solid ammonium sulphate, an aqueous solution of ammonium sulphate, and ice. From a consideration of the Phase Rule it follows that these three phases can only be co-existent in equilibrium at the eutectic point, the temperature of which is below 0°C. The net result is that ice melts and more ammonium sulphate dissolves in the water thus produced.

Now the melting of ice involves the absorption of heat, and in addition the solution of salts in water also usually involves an absorption of heat, so that the process described above causes the temperature of the system to fall progressively until either the solid ammonium sulphate, or the ice, disappears. In the case of practical freezing mixtures, large proportions of the solid salt and ice are purposely employed with the result that the temperature of the system falls until the temperature of the eutectic is finally reached, and the freezing mixture remains at the eutectic temperature until the absorption of heat from the surroundings causes either all the salt to dissolve or, alternatively, all the ice to melt, when, there being

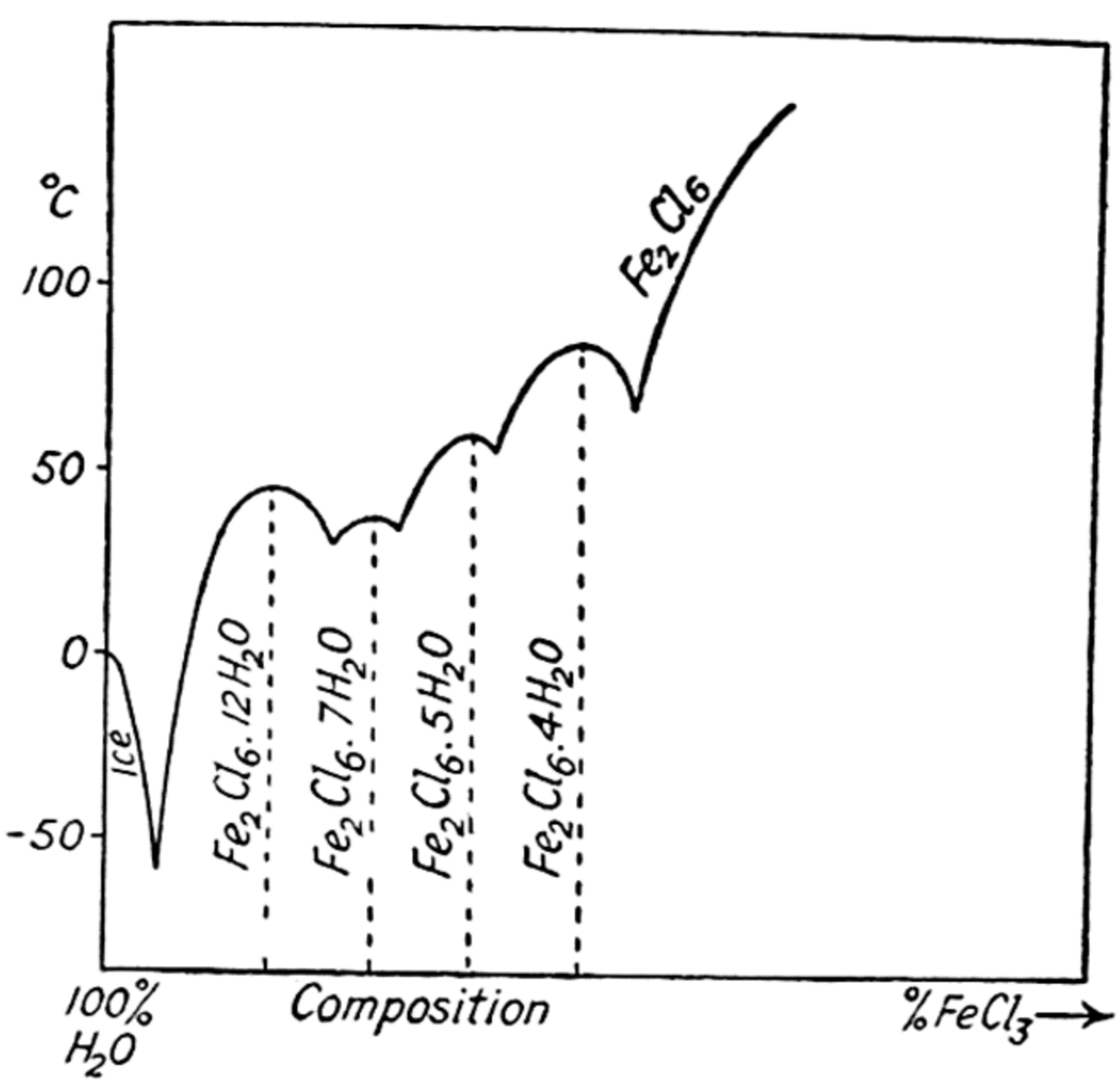


FIG. 83. Salt Hydrates of the System Ferric Chloride-Water

only two phases present, the system is univariant and so the temperature of the mixture rises.

The details of some common freezing mixtures are given below in Table 36.

TABLE 36

Freezing Mixtures

Eutectic Temperature (°C)	Percentage Composition by Weight
− 15	50 NH_4NO_3 : 50 H_2O
− 17	60 $Na_2SO_4,10H_2O$: 40 H_2O
− 18	34 NaCl : 66 Ice
− 20	50 NH_4NO_3 : 50 $Na_2CO_3,10H_2O$

There are a number of important systems of salt hydrates with congruent melting points, the system ferric chloride—water being one of the best known; a portion of the liquidus surface of the equilibrium diagram for this system is shown in Fig. 83.

Type 1 (*b*) Systems. The two components of a binary system frequently exhibit partial solid solubility and in the case of many alloy systems this phenomenon is not only very common, but it has also important technological implications. The thermal equilibrium diagrams for such systems are of two types—

(i) Those in which a eutectic occurs,
(ii) Those in which a peritectic occurs.

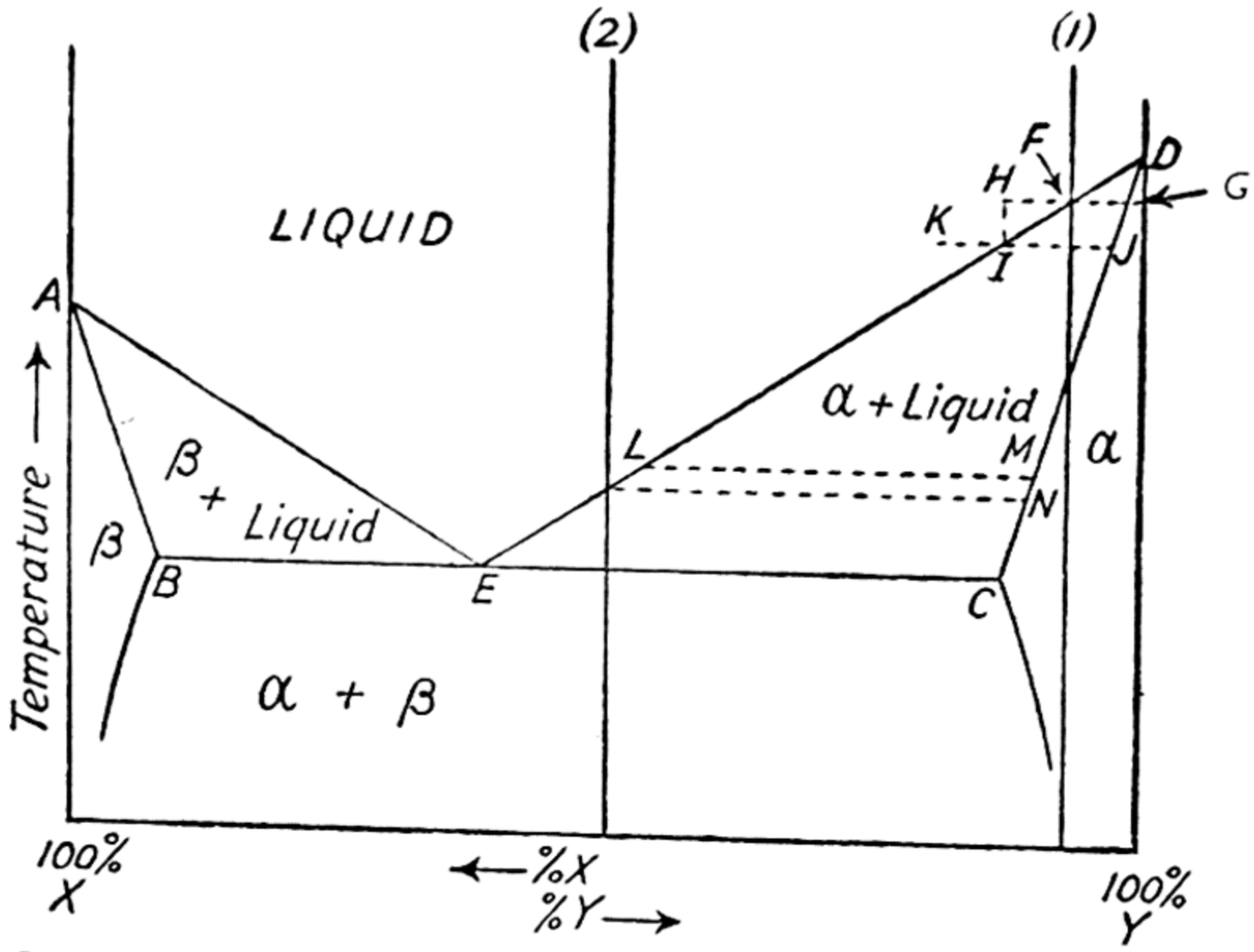


FIG. 84. Equilibrium Diagram for Two Substances, *X* and *Y* which are Completely Soluble in one another in the Liquid State, and Partially Soluble in one another in the Solid State

(i) *Systems in which a Eutectic occurs.* The thermal equilibrium diagram for a binary system of two components exhibiting complete liquid solubility and partial solid solubility is shown in Fig. 84. The two solid solutions formed are termed the α solid solution (that in which metal *Y* acts as solvent and metal *X* as solute), and the β solid solution (that in which metal *X* serves as solvent and metal *Y* the solute). The liquidus is *AED*, and the solidus, *ABECD*. It will be noted that the eutectic horizontal stops short at the saturation limits of the two solid solutions, that is at the points *B* and *C*.

When alloy (1) cools down to the point *F*, crystals of the α solid solution of composition *G* are deposited. This results in an enriching of the residual liquid in metal *X*; for the purpose of the present discussion a change in liquid composition to the point *H* will be imagined. It should however be

carefully noted that the distance *HF* in practice is exceedingly small, a large change in liquid composition being described here only to make the mechanism of the cooling process more evident. Now liquid melt of the composition *H* may persist in the liquid state down to the temperature of the point *I* when crystals of the α solid solution of composition *J* are deposited on top of those initially deposited and of composition *G*. Thus, little by little, the composition of the residual liquid changes down the slope of the liquidus curve *DE* whilst the composition of the α solid solution changes down the branch of the solidus *DC*. By this process the crystals of the α solid solution vary in chemical composition from the innermost core to the outermost skin, being richer in metal *Y* in the core than at the skin of each individual crystal; this phenomenon is known as

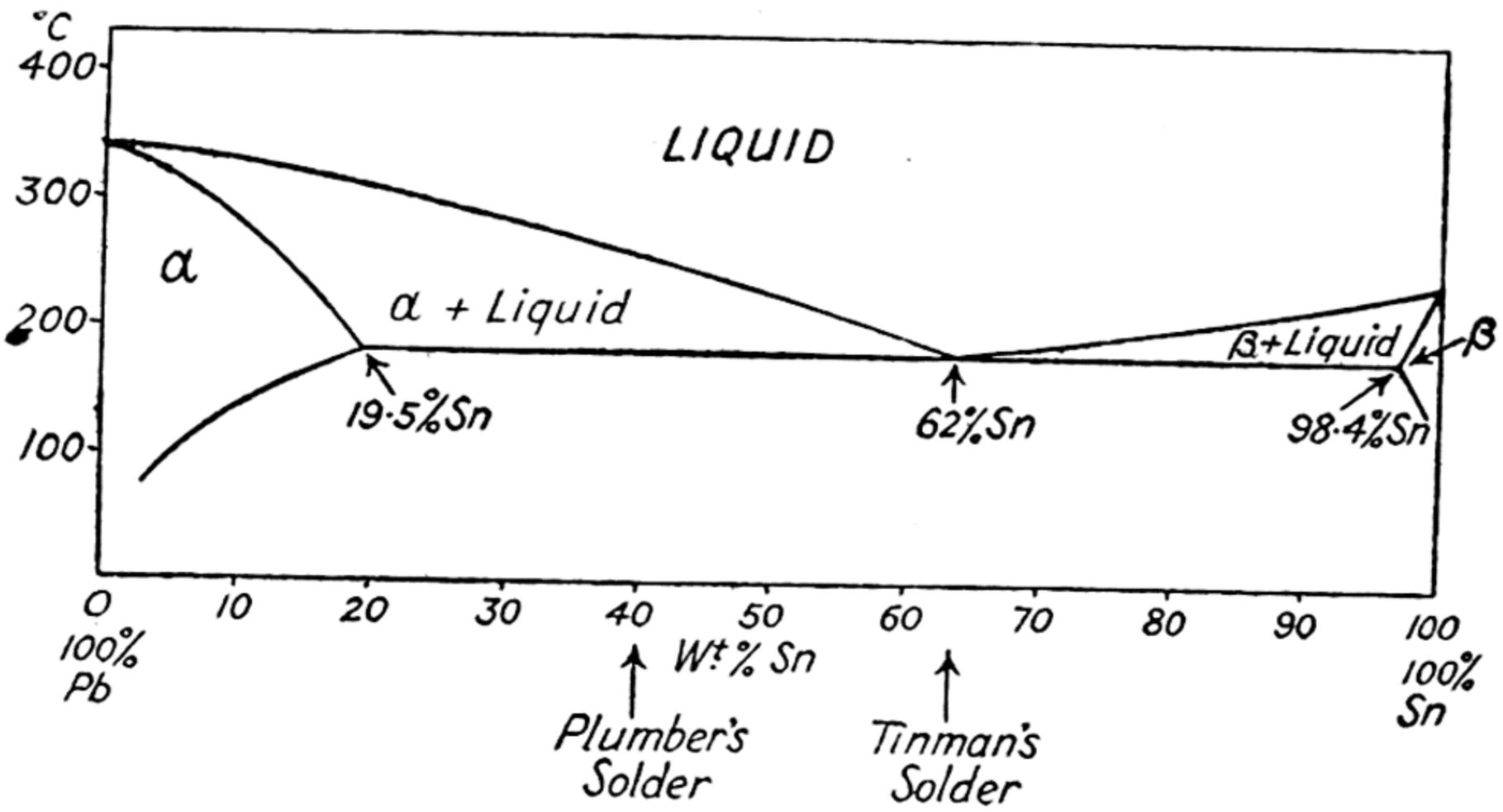


FIG. 85. Lead-Tin Equilibrium Diagram

coring. The process of crystallization of the α solid solution continues until the liquid attains a composition such as that of the point *L* when the last drop of liquid alloy of this composition is absorbed in the solid solution. Thus, the composition of each individual crystal varies from composition *G* in the core to composition *M* at the skin; the average composition of the crystals, however, is that indicated by the vertical line designated (1).

In the case of alloy (2) the α solid solution first deposited is that of composition *N*; thereafter the composition of the α solid solution changes down the slope of the solidus branch to the point *C*, whilst the composition of the liquid alloy changes down the liquidus towards the eutectic point *E*. At the eutectic point there are three phases present in equilibrium, the α and β solid solutions of compositions *C* and *B* respectively, and the liquid alloy of composition *E*. The liquid alloy deposits crystals of the α and β solutions of compositions *C* and *B* until all the liquid has been used up when, there being only two phases present, the system is univariant and

the temperature may fall. In the completely solid condition, therefore, alloy (2) consists of primary crystals of the cored α solid solution, surrounded by the eutectic mixture made up of the two solid solutions of compositions *C* and *B*.

Examples of alloy systems of the type described above are provided by the lead-tin, lead-antimony, copper-silver, and the cadmium-zinc systems. Other systems of this type are silver chloride-cuprous chloride, silver iodide-mercuric iodide, and naphthalene-monochloracetic acid. The lead-tin equilibrium diagram is shown in Fig. 85 and in Plate I the microstructures of two common alloys in this system are shown.

(ii) *Systems in which a Peritectic occurs.* Certain binary systems in which complete liquid solubility and partial solid solubility are exhibited

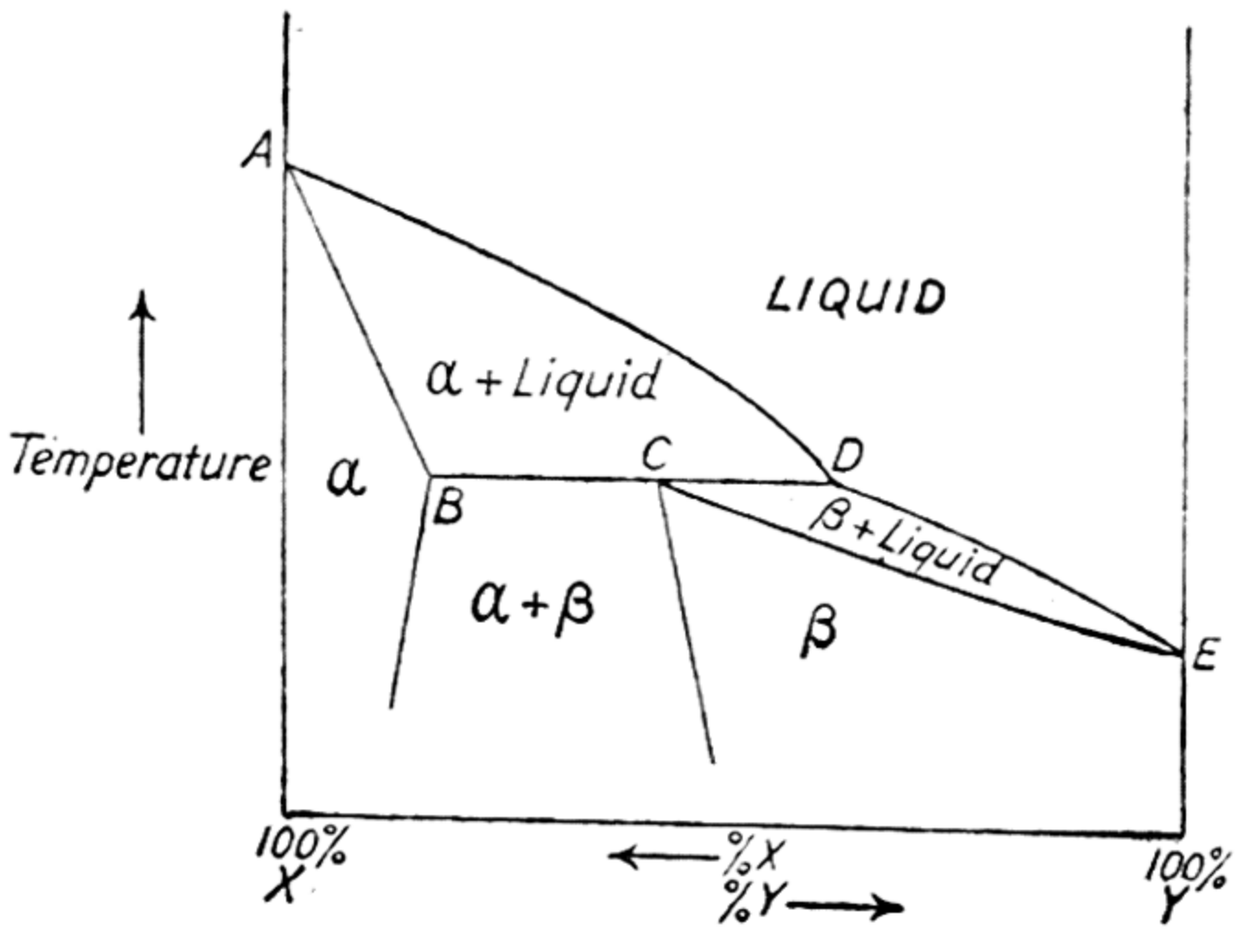


FIG. 86. Equilibrium Diagram showing Peritectic Transformation

do not have a eutectic, but undergo a transformation known as a *peritectic transformation.* A typical equilibrium diagram for this type of system is shown in Fig. 86. The liquidus is *ADE* and the solidus *ABCE.* When any melt of composition between the point *B* and *D* is allowed to cool from the liquid state, the liquid alloy ultimately attains the composition of the point *D*; this is the peritectic point at which there are present simultaneously the two solid solutions designated α and β and liquid alloy of composition *D*. By the arguments of the Phase Rule the temperature must remain constant until one of these three phases disappears. If the composition lies between the points *B* and *C* the α solid solution is deposited until the liquid attains the composition of the point *D*. At this point this liquid melt is absorbed by diffusion into the initially deposited α solid solution, transforming it into the β solid solution of composition *C*. This is the peritectic transformation. When the composition of the initial melt lies between *C* and *D*, the initial solid is the α solid solution, which under true equilibrium conditions would be entirely transformed into the

β solid solution; in practice, however, the liquid still in excess after transformation of the outer skins of the initially deposited α solid solution, proceeds to deposit β solid solutions of compositions indicated by the slope of the line CE, until all the liquid is used up. Systems of the type described above include the cadmium-mercury, silver nitrate-sodium nitrate, silver chloride-lithium chloride, and manganese silicate-magnesium silicate systems.

Type 1 (*c*) Systems. Binary systems in which complete solubility is exhibited both in the liquid as well as in the solid states may be subdivided as

(i) Systems in which the freezing point curve has neither maximum nor minimum.

(ii) Systems in which the liquidus passes through a minimum at which liquidus and solidus coincide.

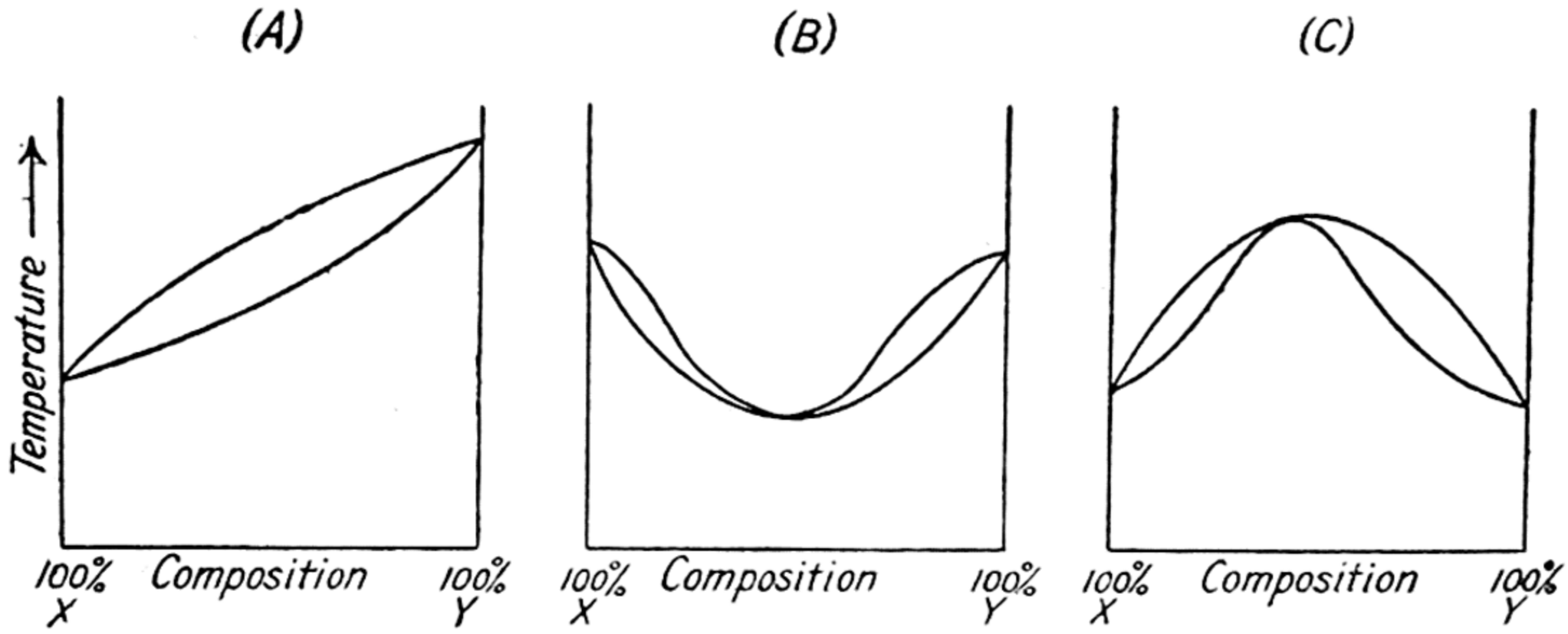


FIG. 87. Equilibrium Diagram for Binary Systems Exhibiting Complete Solubility in both Liquid and Solid States

(iii) Systems in which the liquidus passes through a maximum at which liquidus and solidus coincide.

(i) *Systems in which the Freezing Point Curve has neither Maximum nor Minimum.* The equilibrium diagram for this type of system is depicted in Fig. 87 (*A*) in which the upper curve is the liquidus, and the lower curve the solidus. The cooling of a melt of any composition in systems of this type is similar to that described as alloy (1) in Fig. 84. All melts therefore exhibit coring. A number of important alloy systems are of this type; they include the copper-nickel, silver-platinum, gold-silver, and the platinum-rhodium systems. Other examples include the silver chloride-sodium chloride, lead chloride-lead bromide and naphthalene-β-naphthol systems.

(ii) *Systems in which the Liquidus passes through a Minimum at which Liquidus and Solidus Coincide.* The equilibrium diagram for this type of system is shown in Fig. 87 (*B*). This type of system may be regarded as being built up of two diagrams of the type shown in Fig. 87 (*A*). Examples

of systems of this type include the copper-manganese, copper-gold, nickel-palladium, potassium bromide-potassium chloride, potassium carbonate-sodium carbonate, and *p*-chloriodobenzene-*p*-di-chlorobenzene systems.

(iii) *Systems in which the Liquidus passes through a Maximum at which Liquidus and Solidus Coincide.* The equilibrium diagram for this type of systems is shown in Fig. 87 (*C*). Examples of this type of equilibria are vary rare and confined to some few organic systems.

Type 2 (*a*) Systems. Fig. 88 shows the equilibrium diagram for systems of this type. The similarity of the portion of this diagram designated *CFD*

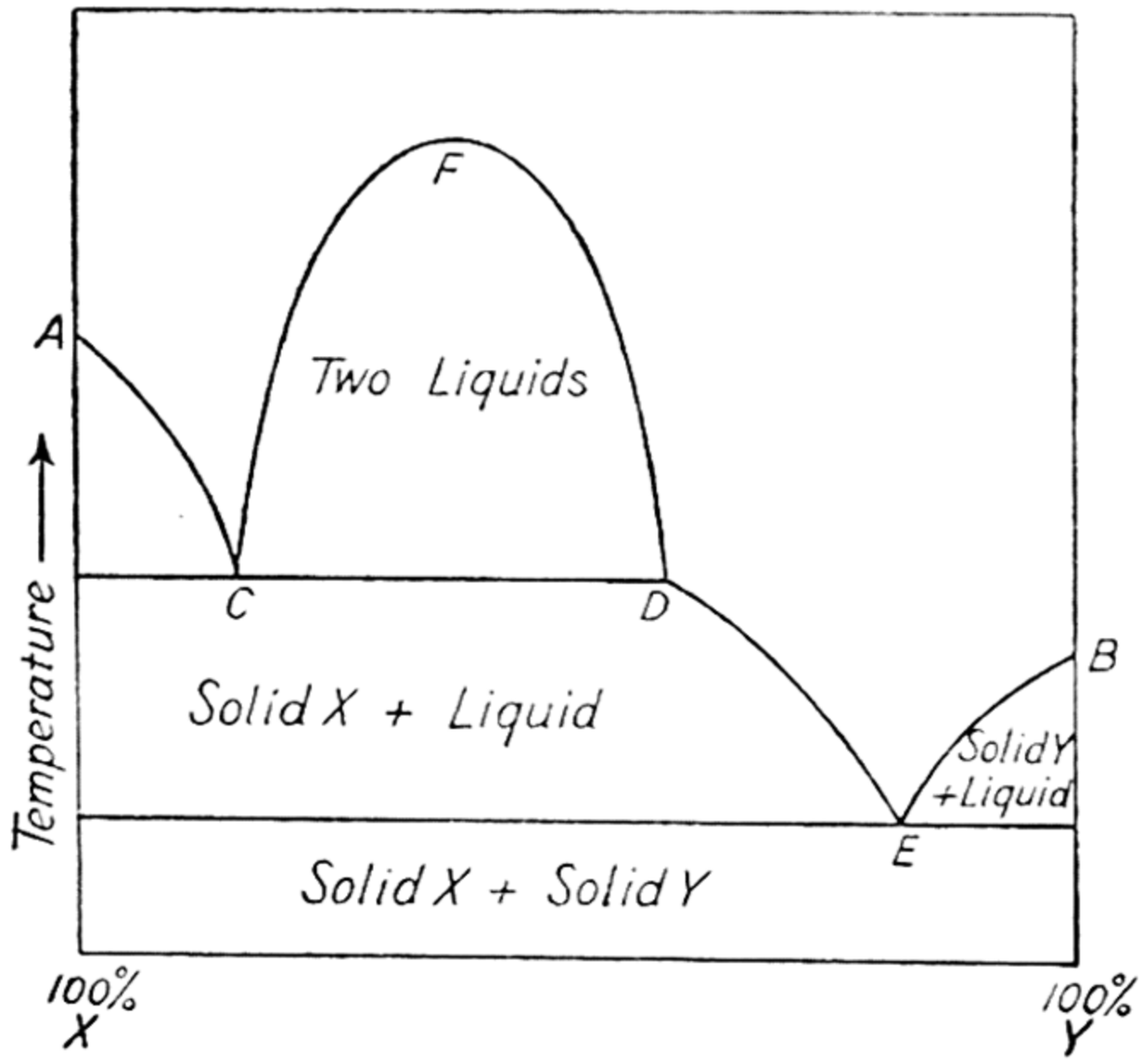


FIG. 88. Equilibrium Diagram for Two Substances, *X* and *Y*, Partially Soluble in the Liquid State and Completely Insoluble in the Solid State

to the phenol-water system (Fig. 73) should be noted; the same arguments regarding conjugate liquid solutions apply, thus *C* and *D* are one pair of conjugate liquid solutions. Within the area enclosed by the curve *CFD* two liquids co-exist. The copper-lead system typifies this type of equilibrium.

Type 2 (*b*) Systems. Just as systems of the type shown in Fig. 84 may be regarded as being a development of systems of the type shown in Fig. 76, by the introduction of the concept of solid solubility, so systems of the type 2 (*a*) may be modified to include solid solutions.

GAS-SOLID SYSTEMS

In discussing the equilibria obtaining in gas-solid systems it is useful to distinguish between—

(*a*) Gas-solid systems in which the gas and the solid react together to form one or more compounds, and

(*b*) Gas-solid systems in which the gas dissolves in the solid.

(*a*) **Gas-Solid Systems in which there is Compound Formation.** One of the simplest examples of this type of equilibrium is that of calcium oxide and carbon dioxide

$$CaO + CO_2 \rightleftharpoons CaCO_3$$

In this system there are two components, CaO and CO_2, and at equilibrium there are three phases. Thus, by application of the Phase Rule—

$$\begin{aligned} F &= C - P + 2 \\ &= 2 - 3 + 2 \\ &= 1 \end{aligned}$$

The system is therefore univariant so that only one variable (e.g. temperature) need be quoted to define the system. In other words, at each specific

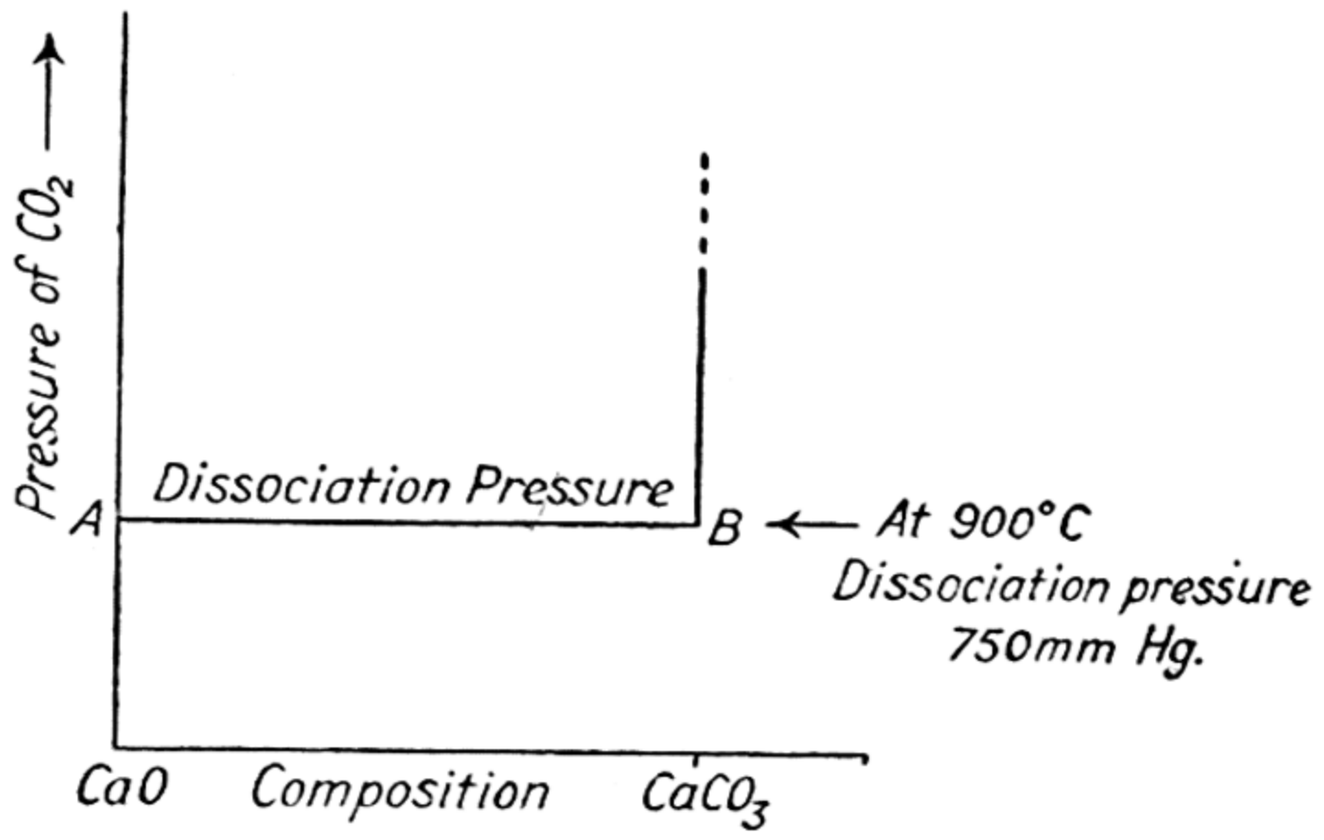


FIG. 89. Dissociation of Calcium Carbonate

temperature the pressure of CO_2 in equilibrium with the CaO and the $CaCO_3$ should be constant and independent of the amounts of the two solid phases present. This equilibrium pressure, characteristic for each pressure, is termed the *dissociation pressure*. If the pressure of carbon dioxide in contact with CaO and $CaCO_3$ is maintained less than the dissociation pressure, the $CaCO_3$ will undergo complete dissociation; on the other hand, if the pressure in the system is maintained higher than the dissociation pressure the CaO will react with the CO_2 to form $CaCO_3$, either until all the CaO is thus converted, or alternatively until the pressure in the system falls; these facts are depicted in graphical form in Fig. 89. In those cases where a metallic oxide reacts with CO_2 to form more than one compound there will obviously be more than one constant pressure stage such as *AB* (Fig. 89).

A similar example of this type of system is that provided by the hydrates of copper sulphate. As progressive dehydration of $CuSO_4 . 5H_2O$ takes

place the vapour pressure decreases suddenly at the composition of each new hydrate; this is shown in Fig. 90.

Deliquescence and Efflorescence

From the foregoing discussion it follows that the stability of a salt hydrate is dependent upon the partial pressure of water with which the hydrate is in contact. If a salt hydrate is maintained in air in which the vapour pressure of water is greater than the vapour pressure of a saturated solution of the highest hydrate of this salt, the solid hydrate will take up water from the atmosphere until ultimately it takes up enough water to form its own unsaturated solution. In other words, this salt hydrate is said to *deliquesce*.

On the other hand if a salt hydrate exists in an atmosphere in which the partial pressure of water vapour is less than the vapour pressure of the salt hydrate system, dehydration of the hydrate will occur and the salt is said to *effloresce*. These two phenomena of deliquescence and efflorescence may be further exemplified by reference to three specific salts, calcium chloride, sodium sulphate and copper sulphate.

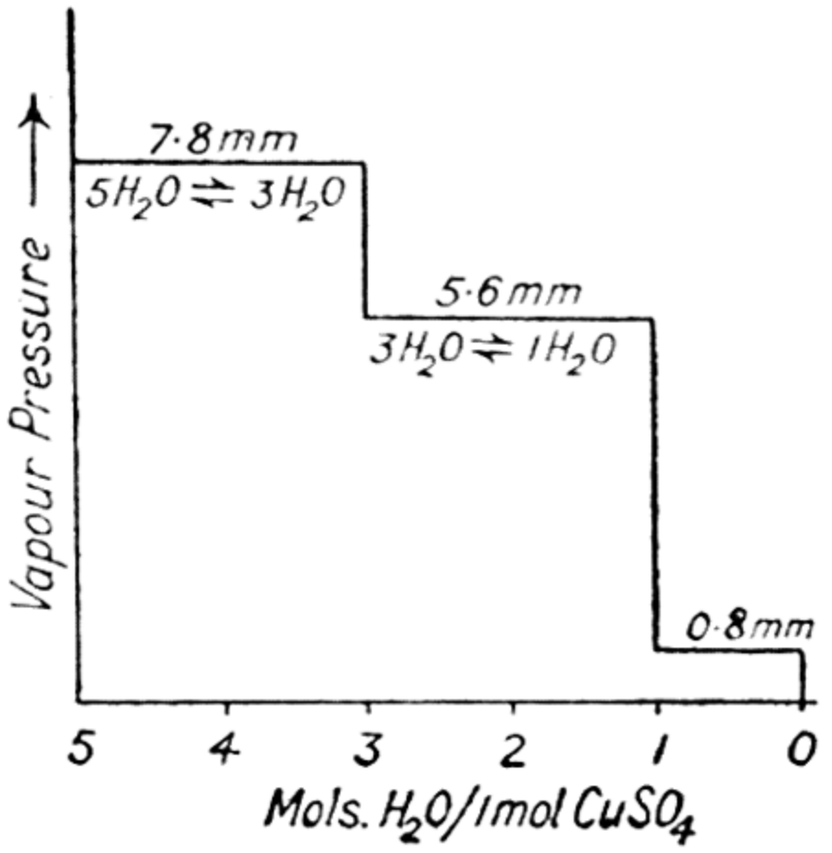


FIG. 90. Dehydration of Copper Sulphate at 25°C

In the case of calcium chloride, the vapour pressure of the hexahydrate, $CaCl_2 . 6H_2O$ is considerably lower than the partial pressure of water vapour in the atmosphere under normal conditions so that this hydrate will absorb moisture, ultimately forming its saturated aqueous solution. But since the vapour pressure of this saturated solution is also lower than the partial pressure of water vapour in the atmosphere, the absorption of water continues until, finally, the solution becomes so diluted that its vapour pressure is the same as the vapour pressure of water in the atmosphere. Calcium chloride is thus a compound capable of deliquescence in air under normal conditions.

Sodium sulphate decahydrate, $Na_2SO_4 . 10H_2O$, has a vapour pressure slightly in excess of the partial pressure of water in the atmosphere on dry days so that dehydration of the decahydrate occurs, that is, the decahydrate effloresces.

In the case of copper sulphate pentahydrate, $CuSO_4 . 5H_2O$, the vapour pressure of water vapour in the atmosphere under normal conditions is less than the vapour pressure of a saturated aqueous solution of this salt so that deliquescence cannot occur, whilst since the vapour pressure of the pentahydrate is lower than the vapour pressure of water vapour in the atmosphere, efflorescence cannot occur either. Copper sulphate trihydrate,

$CuSO_4 . 3H_2O$, and monohydrate, $CuSO_4 . H_2O$, both have lower vapour pressures than the pentahydrate (*see* Fig. 90), so that the monohydrate and the trihydrate are both capable of absorbing moisture from the atmosphere to form the pentahydrate, but there the absorption process stops and the pentahydrate remains as a dry solid since the vapour pressure of the saturated solution is greater than the vapour pressure of water in the atmosphere. It is, however, most important to appreciate that deliquescence and efflorescence are relative properties; for example, in a very dry atmosphere $CuSO_4 . 5H_2O$ would effloresce, whilst in a very moist atmosphere $Na_2SO_4 . 10H_2O$ would deliquesce.

(*b*) **Gas—Solid Systems in which the Gas Dissolves in the Solid.** If the gas dissolves in the solid two phases will be present, the gas and the solid

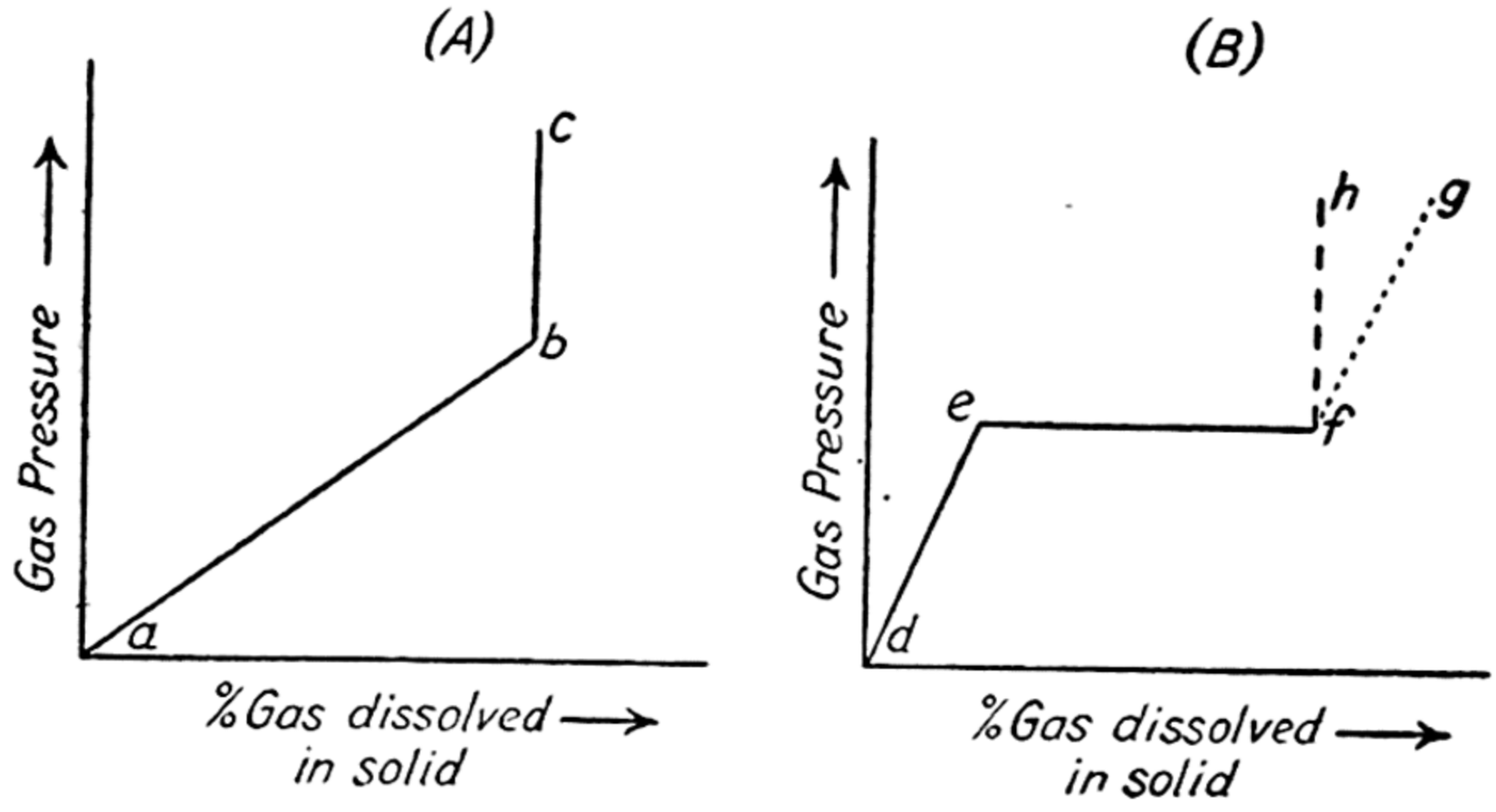


FIG. 91. Gas Pressure—Composition Diagram for Solutions of Gases in Solids

solution of the gas in the solid. By application of the Phase Rule, therefore—

$$\begin{aligned} F &= C - P + 2 \\ &= 2 - 2 + 2 \\ &= 2 \end{aligned}$$

from which it will be noted that the system is bivariant so that at constant temperature the composition of the solid solution will vary with variation in the pressure of the gas. Thus solution of the gas in the solid continues until it saturates the solid when, since no more gas can dissolve, the pressure in the system increases rapidly. On the other hand, it is possible that when the solid solution of the gas in the solid has attained a certain critical composition the single solid solution may either split up into two solid solutions, or alternatively, chemical combination between the solid solution and the gas may occur when a pressure equal to the dissociation pressure is reached.

When simple solution of the gas in the solid takes place, the relationship between gas pressure and the composition of the solid solution may be represented by a straight line, portion *ab* in Fig. 91 (*A*); in this diagram the point *b* corresponds to the formation of a saturated solid solution after which the gas pressure increases rapidly as indicated by portion *bc*. When two solid solutions are formed, there are three phases present, the two solid solutions and the gas, thus—

$$\begin{aligned} F &= C - P + 2 \\ &= 2 - 3 + 2 \\ &= 1 \end{aligned}$$

and the system is univariant; in other words, if the temperature is fixed, the pressure and the composition of the phases are also fixed. The relationship between gas pressure and concentration is that shown in Fig. 91 (*B*), in which the portion *de* represents the formation of the first solid solution, and the portion *ef*, parallel to the concentration axis, the condition obtaining when the second solid solution makes its appearance. If, as the concentration of gas is increased one of these solid solutions disappears, say by conversion into the second solid solution, then since there would again be only two phases present, the curve would assume the form indicated by *fg*. But, if chemical combination occurs between the solid solutions the gas pressure will increase sharply at the composition corresponding to the compound composition; this is represented by the portion *fh*.

CHAPTER 10

THERMOCHEMISTRY

CHEMICAL reactions are usually associated with the liberation or, alternatively, with the absorption of heat. When either elements or compounds react together very readily, as do chlorine and phosphorus, energy is liberated in the form of light as well as of heat.

Chemical compounds may be classified into two groups: (*a*) those compounds which are formed from their elements with the liberation of heat (e.g. phosphorus trichloride, carbon dioxide, hydrogen chloride and sulphur dioxide); these are termed *exothermic compounds*, and (*b*) those compounds formed from their elements with the absorption of heat (e.g. carbon disulphide, nitric oxide, acetylene); these are termed *endothermic compounds*.

HEAT OF REACTION

The *heat of reaction* of a chemical change is the quantity of heat, measured in calories, which is liberated or absorbed when the number of molecules of reactants indicated by the chemical equation have completely reacted. It is thus possible to write equations in a more complete form so as to include the heat changes involved. This is typified by the following equations.

$$2Na + 2HCl = 2NaCl + H_2 + 152\,540 \text{ cal.} \quad . \quad . \quad (1)$$

$$C + O_2 = CO_2 + 94\,450 \text{ cal.} \quad . \quad . \quad . \quad . \quad (2)$$

It should be noted that the heats of reaction involved are not independent of external conditions. Thus, if gases react together it is necessary to know if they do so at constant volume or at constant pressure; in the former case no external work is done by or against the atmosphere, whereas in the latter case work is done either by or against the atmosphere so that the thermal equivalent of this work must be added to, or subtracted from, the heat of reaction at constant volume.

The physical state of the reacting substances or the products also affects the heat of reaction, and in order to prevent confusion it is necessary to specify the physical states of reactants and of products using the symbols (*s*), (*l*) and (*g*) to indicate the solid, liquid and gaseous states respectively. Thus the following equation

$$Na(s) + \tfrac{1}{2}Cl_2(g) = NaCl(s) + 98\,330 \text{ cal.} \quad . \quad . \quad (3)$$

indicates that 23 g of solid sodium react with 35·46 g of gaseous chlorine

to produce 58·46 g of solid sodium chloride accompanied by the liberation of 98 330 calories of heat.

When hydrogen and oxygen combine together the heat of reaction will differ according as to whether the product is water vapour or steam, the larger quantity of heat being associated with the formation of steam because of the liberation of the additional heat associated with the latent heat of vaporization of water; the two heat values are given in the following thermochemical equations.

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g) + 57\,801 \text{ cal.} \quad . \quad . \quad . \quad (4a)$$

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l) + 68\,470 \text{ cal.} \quad . \quad . \quad . \quad (4b)$$

In dealing with elements capable of existence in differing allotropic forms it is necessary to state which allotrope is involved since different allotropes of the same element have different heats of reaction. For example, when monoclinic sulphur (S_β) is converted to rhombic sulphur (S_α), heat is liberated—

$$S_\beta \rightarrow S_\alpha + 75 \text{ cal.} \quad . \quad . \quad . \quad . \quad (5)$$

The heat of reaction is also dependent upon the temperature at which the reaction is conducted. Unless mention is made to the contrary it is assumed that the reaction commences at atmospheric temperature, to which the temperature of the products subsequently returns.

Heat of Formation

The quantity of heat, measured in calories, evolved or absorbed when one gramme molecular weight of a compound is produced from its component elements, is known as the *heat of formation* of the compound. The heats of formation of some common compounds are shown in Table 37 on p. 204.

From the table shown on p. 204 it should be noted that liberation of heat is associated with the formation of exothermic compounds (e.g. CO_2), whilst abstraction of heat is associated with the formation of endothermic compounds (e.g. C_2H_2).

Heat of Combustion

The heat liberated when one gramme molecular weight of an element or a compound burns completely in air or in oxygen is termed its *heat of combustion*. The following thermochemical equations include the appropriate heats of combustion.

$$C(s) + O_2(g) = CO_2(g) + 94\,450 \text{ cal.}$$

$$S(s) + O_2(g) = SO_2(g) + 70\,920 \text{ cal.}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g) + 57\,801 \text{ cal.}$$

$$C_2H_2(g) + 2\tfrac{1}{2}O_2(g) = 2CO_2(g) + H_2O(g) + 300\,601 \text{ cal.}$$

TABLE 37

Heats of Formation

(*in calories per gramme mol at* 18°*C*)

Substance	Heat of Formation, $-\Delta H$
CO (*g*)	+ 26 840
CO_2 (*g*)	+ 94 450
SO_2 (*g*)	+ 70 920
SO_3 (*s*)—β form	+ 105 200
H_2O (*g*)	+ 57 801
H_2O (*l*)	+ 68 370
HF (*g*)	+ 64 000
HCl (*g*)	+ 22 060
HBr (*g*)	+ 8 650
HI (*g*)	− 5 910
NO (*g*)	− 21 600
NO_2 (*g*)	− 8 030
N_2O (*g*)	− 19 650
C_2H_2 (*g*)	− 53 900
C_2H_4 (*g*)	− 11 000
NH_3 (*g*)	+ 11 000
CS_2 (*l*)	− 15 400
H_2S (*g*)	+ 5 300
P_2O_5 (*s*)	+ 36 000

$$CS_2(g) + 3O_2(g) = CO_2(g) + 2SO_2(g) + 258\ 290 \text{ cal.}$$

$$CO(g) + \tfrac{1}{2}O_2(g) = CO_2(g) + 67\ 610 \text{ cal.}$$

Thus, in the first example, 94 450 cal. represents the heat of combustion of one gramme molecular weight of carbon, that is, 12 g of carbon; similarly, 70 920 cal. represents the heat of combustion of one gramme molecular weight of sulphur; 300 601 cal. the heat of combustion of one gramme molecular weight of acetylene, and 67 610 cal. the heat of combustion of one gramme molecular weight of carbon monoxide. It should be noted that the heats of combustion of carbon, sulphur and hydrogen also represent the heats of formation of carbon dioxide, sulphur dioxide and water vapour respectively.

Heat of Solution

Heat is either liberated or absorbed when a substance dissolves in a solvent. When making calculations involving reactions in solution it is therefore necessary to take these facts into account. The *heat of solution* is the quantity of heat liberated or absorbed when one gramme molecular

weight of a substance is dissolved in such a large volume of the solvent that further addition of solvent causes no further heat change. When such dilute solutions are prepared with water as the solvent it is customary to employ the symbol "aq" to indicate this fact.

Heat of Neutralization

Heat is also evolved when in aqueous solution a base is neutralized by an acid, and vice versa. The *heat of neutralization* of an acid is defined as the amount of heat evolved when one gramme equivalent weight of the acid is neutralized by a base.

Some values for heats of neutralization for a number of acids are given in Table 38.

TABLE 38

Heats of Neutralization

Base	Acid	Heat of Neutralization (calories)
NaOH, aq	HCl, aq	+ 13 710
KOH, aq	HCl, aq	+ 13 710
$\frac{1}{2}Ca(OH)_2$, aq	HCl, aq	+ 13 717
$\frac{1}{2}Ba(OH)_2$, aq	HCl, aq	+ 13 708
NaOH, aq	HNO_3, aq	+ 13 710
KOH, aq	HNO_3, aq	+ 13 710
$\frac{1}{2}Ca(OH)_2$, aq	HNO_3, aq	+ 13 710
$\frac{1}{2}Ba(OH)_2$, aq	HNO_3, aq	+ 13 710
NaOH, aq	$\frac{1}{2}H_2SO_4$, aq	+ 14 241
KOH, aq	$\frac{1}{2}H_2SO_4$, aq	+ 14 240
$\frac{1}{2}Ca(OH)_2$, aq	$\frac{1}{2}H_2SO_4$, aq	+ 14 240
$\frac{1}{2}Ba(OH)_2$, aq	$\frac{1}{2}H_2SO_4$, aq	+ 14 240
NaOH, aq	HF, aq	+ 16 210
KOH, aq	HF, aq	+ 16 210
$\frac{1}{2}Ca(OH)_2$, aq	HF, aq	+ 16 210
$\frac{1}{2}Ba(OH)_2$, aq	HF, aq	+ 16 210
NH_4OH, aq	HCl, aq	+ 12 045
NH_4OH, aq	HNO_3, aq	+ 12 170
NH_4OH, aq	$\frac{1}{2}H_2SO_4$, aq	+ 12 685
NH_4OH, aq	HF, aq	+ 15 100
NaOH, aq	HCN, aq	+ 2 711
KOH, aq	HCN, aq	+ 2 840
$\frac{1}{2}Ca(OH)_2$, aq	HCN, aq	+ 2 840
$\frac{1}{2}Ba(OH)_2$, aq	HCN, aq	+ 2 880
NH_4OH, aq	HCN, aq	+ 1 300

Hess's Law of Constant Heat Summation

This law states that *the heat evolved or absorbed during any chemical reaction is independent of the number of stages by means of which the reaction is carried out, being dependent only upon the initial reactants and the final products of the reaction.* Hess's Law may be illustrated by reference to the formation of carbon dioxide either directly from its component elements, or via the formation of intermediary carbon monoxide.

(A) Formation of Carbon Dioxide Direct from its Component Elements.

$$\underset{12\text{ g}}{C(s)} + \underset{32\text{ g}}{O_2(g)} = \underset{44\text{ g}}{CO_2(g)} + 94\,450\text{ cal.}$$

(B) Formation of Carbon Dioxide via the Formation of Intermediate Carbon Monoxide.

$$\text{(i)}\quad \underset{12\text{ g}}{C(s)} + \underset{16\text{ g}}{\tfrac{1}{2}O_2(g)} = \underset{28\text{ g}}{CO(g)} + 26\,840\text{ cal.}$$

$$\text{(ii)}\quad \underset{28\text{ g}}{CO(g)} + \underset{16\text{ g}}{\tfrac{1}{2}O_2(g)} = \underset{44\text{ g}}{CO_2(g)} + 67\,610\text{ cal.}$$

Thus, in equation (*A*) the oxidation of 12 g of solid carbon by 32 g of gaseous oxygen to 44 g of gaseous carbon dioxide is associated with the evolution of 94 450 cal.; whilst the oxidation of 12 g of solid carbon in the two-step process as indicated in equations (*B*) (i) and (ii) by a total weight of 32 g of oxygen still leads to the formation of 44 g of carbon dioxide and the evolution of the same quantity of heat, that is, 94 450 cal. (26 840 + 67 610).

Another illustration of Hess's Law is provided by the syntheses of an aqueous solution of ammonium chloride, a compound capable of being prepared in two distinctly different ways—

(1) *The Reaction of Gaseous Ammonia and Gaseous Hydrogen Chloride to form Solid Ammonium Chloride as follows—*

$$(a)\quad NH_3(g) + HCl(g) = NH_4Cl(s) + 41\,890\text{ cal.}$$

If this one gramme molecular weight of ammonium chloride is dissolved in water there is an absorption of heat amounting to 3818 cal., thus—

$$(b)\quad NH_4Cl(s) + \text{aq} = NH_4Cl,\text{ aq} - 3818\text{ cal.}$$

The production of an aqueous solution containing one gramme molecular weight of ammonium chloride is therefore associated with the liberation of (41 890 − 3818) cal. = + 38 072 cal.

(2) *The Reaction of Gaseous Hydrogen Chloride with an Aqueous Solution of Ammonia.* The solution of ammonia in water, the solution of hydrogen chloride in water, and the subsequent reaction of hydrochloric acid with the ammonium hydroxide are all exothermic reactions as is indicated below.

$$(c) \quad NH_3(g) + aq = NH_3, aq + 8\,350 \text{ cal.}$$
$$(d) \quad HCl(g) + aq = HCl, aq + 17\,627 \text{ cal.}$$
$$(e) \quad NH_3, aq + HCl, aq = NH_4Cl, aq + 12\,095 \text{ cal.}$$
$$\text{Total heat liberated} = + 38\,072 \text{ cal.}$$

Thus, the heat liberated as the algebraic sum of reactions (*a*) and (*b*) is equal to the sum of the heat liberated in reactions (*c*) + (*d*) + (*e*); in other words, the synthesis of an aqueous solution of ammonium chloride by different methods leads to the liberation of the same quantity of heat.

CALORIFIC VALUES OF FUELS

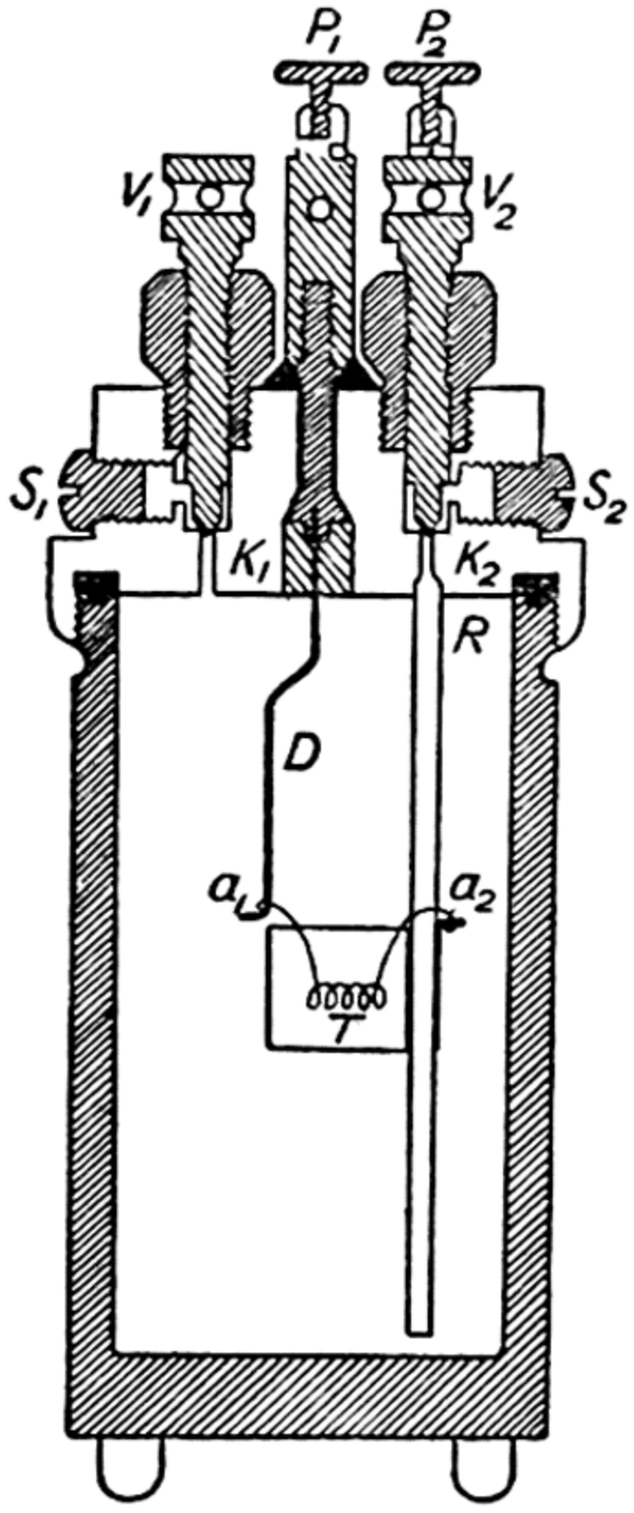
The calorific value of a fuel is the quantity of heat produced by the combustion of unit part by weight of a fuel, and may be expressed in terms of various heat units. For example, the calorie is the quantity of heat required to raise 1 g of water through 1°C, the calorific value being reported in calories per gramme. The "large calorie" or "kilogramme calorie" is equal to 1000 g. cal. For engineering purposes calorific values are often quoted in "British Thermal Units" (B.Th.U.) per lb; in this system, one unit is defined as the quantity of heat necessary to raise 1 lb of water through 1°F. A third unit is the "Centigrade Heat Unit," (C.H.U.) which is the quantity of heat required to raise 1 lb of water through 1°C. These units are readily interconverted, using the following conversion factors

$$1 \text{ kg cal} = 2{\cdot}2 \text{ C.H.U.} = 3{\cdot}96 \text{ B.Th.U., and}$$
$$1 \text{ cal/g} = 1 \text{ kg cal/kg} = 1{\cdot}8 \text{ B.Th.U./lb.}$$

Solid Fuels

For the determination of the calorific value of solid fuels a known weight (of the order of 1 g) of the fuel is burnt in oxygen at a pressure 25 to 35 atmospheres within a closed vessel known as a "bomb." The bomb is immersed in water contained within a calorimeter and on combustion occurring the temperature rise of the water contained within the calorimeter is proportional to the heat generated by the fuel, and thus to its calorific value. The fuel is fired electrically from outside the bomb by heating to white heat a short length of fine wire.

The bomb itself is fabricated from strong alloy steel and is composed of two principal parts, the body and the cap (*see* Fig. 92). In order to ensure a gas-tight joint a lead ring is often fitted at the junction of body and cap. Two rods extend into the body of the bomb from the underside of the cap, serving both as crucible supports and also as terminals for the firing wire; one of these rods is insulated electrically from the metal of the cap. In preparation for carrying out a determination, a small loop of firing wire



P₁ and P₂ = Terminals for electrical connections
V₂ = Inlet needle valve
V₁ = Outlet " "
S₁ and S₂ = Screwed plugs fitted when bomb is placed in calorimeter
R = Platinum tube serving as inlet for oxygen and also as electrical connection for firing wire
D = Platinum rod serving as electrical connection for firing wire
T = Silica capsule containing fuel
a₁ and a₂ = Firing wire connected to D and R at these points

FIG. 92. Bomb Calorimeter

(usually nickel but sometimes platinum) is attached to the two supports, the loop itself being embedded in the weighed fuel contained in a crucible supported within a ring at the bottom of one of the above-mentioned rods. The cap is then screwed on to the body of the bomb. Oxygen under pressure is admitted to the bomb through a needle valve in the cap, until the pressure inside the bomb, as indicated by a gauge, is between 25 and 35 atmospheres; the needle valve is then closed, the electrical connexions made but the circuit not completed, and the bomb placed within the calorimeter.

The total water equivalent of the calorimeter should be from 2500 to 3000 g, so that a temperature rise of 2·5°–3·0°C may be obtained. In order to cause the heat loss from the calorimeter to take place at a uniform rate the calorimeter vessel itself should be enclosed in an outer water jacket

containing from 15 to 20 litres of water. The water in the calorimeter vessel is stirred mechanically throughout the determination and its temperature observed each minute by means of a thermometer which may be read to 0·01°C.

When all the preparations as detailed above have been made, the mechanical stirrer is started and after an interval of five minutes the thermometer is read and further readings taken at one minute intervals throughout the determination. The observations may be divided into three groups, (i) the initial period, (ii) the main or firing period, and (iii) the cooling-off or final period. The initial period commences with the first thermometer reading and concludes when the bomb is fired at the end of the fifth minute; the firing period begins with the firing of the bomb and continues until heat transfer from the bomb ceases as indicated by a fall in the thermometer reading. The first reading of the cooling-off period is that immediately following the maximum reading; it is of five minutes duration. Thus, knowing the weight of fuel burnt, the total water equivalent of the calorimeter and the rise in temperature of the water in the calorimeter, the calorific value of the fuel may be calculated.

As well as the carbon in the fuel burning to carbon dioxide, the combustible sulphur, at the high pressures which exist within the bomb, is oxidized to sulphur trioxide which, combining with water formed by the oxidation of the hydrogen in the fuel, gives rise to the production of sulphuric acid. Similarly, the nitrogen in the fuel forms oxides of nitrogen which in the presence of water form nitric acid. The syntheses of both these acids are exothermic processes and the heat evolved must be taken into account when calculating the calorific value of the fuel if accurate results are required. It is with the object of giving protection against these acids that the inner surface of many types of bomb are coated with vitreous enamel or with some corrosion-resistant metal coating such as chromium or even gold.

The bomb calorimeter may also be employed to determine the calorific value of certain types of liquid fuels (e.g. heavy fuel oils) using the same technique as that described above. The calorific value of light and readily volatilized liquid fuels (e.g. petrol) is best determined experimentally by using a modified type of Boys' gas calorimeter.

Example of Calculation of Calorific Value of a Solid Fuel

Nature of sample		Bituminous coal
Weight of sample	=	1·0 g
Weight of water in calorimeter	=	2200·0 g
Water equivalent of bomb, etc.	=	400·0 g
Total weight of water	=	2600·0 g

Initial period		Firing period		Cooling-off period	
Time (min)	Temperature (°C)	Time (min)	Temperature (°C)	Time (min)	Temperature (°C)
0	18·349	6	20·550	10	20·968
1	18·351	7	20·960	11	20·964
2	18·353	8	20·971	12	20·960
3	18·356	9	20·971	13	20·957
4	18·358			14	20·953
5	18·360			15	20·949
Mean temperature during initial period = 18·355°C		Maximum temperature during firing period = 20·971°C			

Observed rise = (20·971 − 18·355°C)	=	2·616°C
Thermometer correction	=	+ 0·008
Corrected rise	=	2·624°C
Heat liberated	=	2·624 × 2600 cal.
Heat liberated by 1 g of sample	=	2·624 × 2600 cal.
	=	6 822 cal.
Calorific value of sample	=	6 822 cal./g
	=	6 822 × 1·8 B.Th.U/lb
	=	12 280 B.ThU/lb

Note: In this example no account has been taken of heat evolution due to the syntheses of sulphuric and nitric acids.

It should also be noted that in the above numerical example no account has been taken of the usual "cooling correction"; for details on this particular point reference should be made to British Standard Specification, No. 1016, 1942.

Gaseous Fuels

The determination of the calorific value of a gaseous fuel is usually carried out by means of the Boys' gas calorimeter, the essential features of which are that heat is abstracted from two luminous jets of burning gas (i.e. the gaseous fuel under examination) by a stream of water flowing through two spiral copper pipes in series which surround the combustion chamber, the whole being surrounded by a metal casing (*see* Fig. 93). The copper pipes are bound with wire to increase their capacity for heat absorption. The temperatures of the inlet and the outlet water are read on thermometers placed at suitable positions in the inlet and outlet jets. The inlet water first passes downwards through the outer coils and then upwards through the inner coils, the latter being heat insulated from the former by a partition. The water finally flows through channels on the exterior of the metal

casing immediately above the chimney, into a mixer formed from coiled brass strips, from whence it leaves the calorimeter. The calorimeter is provided with a movable outlet pipe by means of which the water leaving the apparatus may be directed either to waste or into a large measuring cylinder.

At the commencement of the test, water is poured into the base of the apparatus until it overflows at the spout provided; condensation water

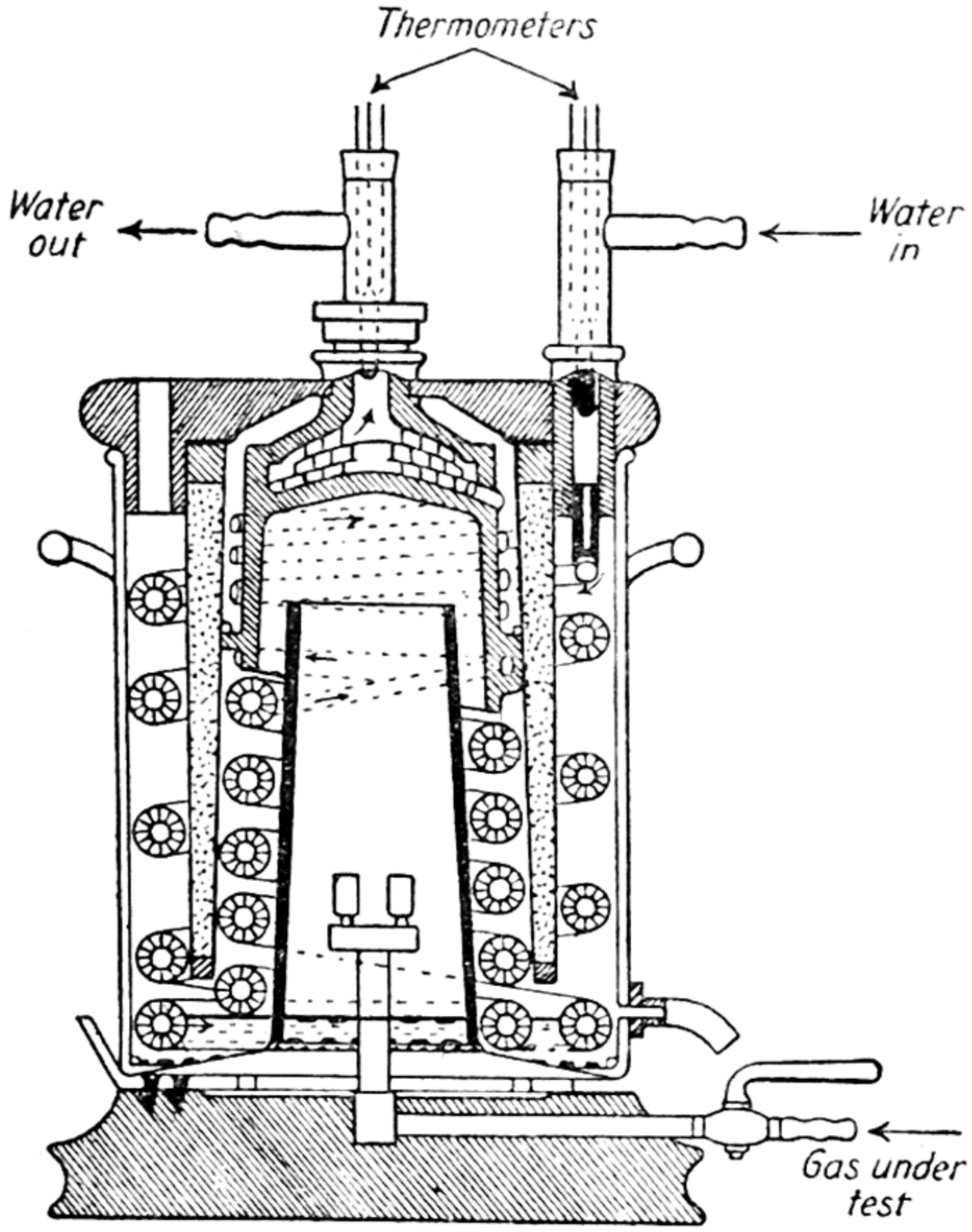


FIG. 93. Boys' Gas Calorimeter

from the burning gas flows from this spout during a test and is collected and measured. An accurate gas meter (a meter giving a complete revolution for each 0·1 ft^3 is very suitable) is connected to the gas supply to be tested, and the calorimeter connected to the gas meter.

In carrying out a test, the gas jets are lighted and the gas flow adjusted to be approximately 0·1 ft^3/min (this rate of flow is suitable for gases such as coal gas, but with gases of lower calorific value a rate of flow three or four times this value should be employed); the rate of water flow is then adjusted so that the products of combustion leave the apparatus as nearly as possible at atmospheric temperature. With a temperature difference of 10°–20°C between inlet and outlet water sufficient cooling of the exit

gases should be effected. Having made these adjustments the apparatus should be allowed to run for 20–30 min before making a test, the outlet water should be allowed to run to waste during this stage. With the commencement of the actual test the temperatures of the inlet and outlet water are read on the appropriate thermometers, and at the same time the outlet pipe is moved so that the outlet water flows into a large measuring cylinder. The inlet water temperature should be read again at the completion of the first, second and third revolutions of the main hand of the gas meter, whilst the temperature of the outlet water should be read at every quarter of a revolution of the main hand of the gas meter. A suitable volume of gaseous fuel for making the test is 0·3 ft^3.

Example of Calculation of Calorific Value of a Gaseous Fuel

Volume of gas burnt = 0·3 ft^3
Volume of condensed water = 6·3 ml
Volume of water flowing through calorimeter during test = 1780·0 ml

Volume of Gas Burnt (ft^3)	Inlet Water Temperature (°C)	Mean Inlet Water Temperature, θ_1 (°C)	Outlet Water Temperature (°C)	Mean Outlet Water Temperature, θ_2 (°C)	$\theta_2 - \theta_1$ (°C)
0·0	9·65	9·63	28·0 28·0 28·0 28·1 28·15	28·05	18·42
0·1	9·60				
0·2	9·55	9·58	28·0 28·1 28·2 28·2	28·13	18·55
0·3	9·56	9·58	28·25 28·25 28·30 28·25	28·27	18·69

Average of differences $(\theta_2 - \theta_1)$ = 18·6°C

Gross calorific value of gas $= \frac{1{\cdot}780 \times 18{\cdot}6}{0{\cdot}3}$ k.cal./ft^3

$= 110{\cdot}4$ k.cal./ft^3

To calculate the net calorific value it is necessary to deduct from the gross calorific value an amount of heat obtained by multiplying the number of millilitres of condensed water per cubic foot of gas used in the test by 0·6 cal. Thus, in this particular example—

$$\text{Net calorific value} = 110{\cdot}4 - \left(\frac{6{\cdot}3}{0{\cdot}3} \times 0{\cdot}6\right) \text{ k.cal./ft}^3$$

$$= 110{\cdot}4 - 12{\cdot}6 \text{ k.cal./ft}^3$$

$$= 97{\cdot}8 \text{ k.cal./ft}^3$$

$$= 97{\cdot}8 \times 3{\cdot}96 \text{ B.Th.U./ft}^3$$

$$= \underline{\underline{387{\cdot}3 \text{ B.Th.U./ft}^3}}$$

Some typical examples of calorific values of solid, liquid and gaseous fuels and their chemical analyses are shown in Table 39 on p. 214.

Intrinsic Energy

From a consideration of the law of conservation of energy, and also from the fact that the formation of exothermic compounds is accompanied by the evolution of heat, it may be argued that an equivalent amount of some other form of energy has been converted into heat. It is thus possible to attribute to each substance a specific *intrinsic energy*, by which term is implied the total amount of energy stored within that substance. The absolute value of the intrinsic energy of an element or a compound, however, is unknown.

The intrinsic energy of an uncombined element in its normal form is customarily assumed to be zero, so that if a compound is exothermic in nature, then the intrinsic energy of that compound must be lower than the sum of the intrinsic energies of the component elements by a quantity of energy equivalent to the heat of formation of that compound. In other words, the intrinsic energy of a compound is equal to its heat of formation with the sign reversed. For example, the intrinsic energy of carbon dioxide, taking the intrinsic energies of carbon (as graphite) and oxygen to be zero, and substituting these values in the following equation, is — 94 450 calories.

$$\begin{aligned} C + O_2 &= CO_2 && + 94\,450 \text{ cal.} \\ \text{Intrinsic energy} &= 0 + 0 = - 94\,450 && + 94\,450 \end{aligned}$$

From the foregoing discussion it should be noted that exothermic compounds possess intrinsic energies which have negative values, whilst conversely, endothermic compounds have intrinsic energies with positive values.

This relationship between the heat of a reaction and the intrinsic energies of reactants and products applied in conjunction with Hess's Law are of considerable value in solving thermochemical calculations.

TABLE 39

Typical Calorific Values

	Calorific Value (net)	C	H	N	S	O	CO_2	CO	CH_4	C_nH_{2m}
Solid fuels										
Anthracite	14 580 B.Th.U./lb	94·0	3·0	1·5		1·5				
Coke	13 100 ,, ,,	95·0	1·0	2·0		2·0				
Bituminous coal	10 670 ,, ,,	61·5	4·5	1·37	1·0	6·63				
Lignite	8 700 ,, ,,	70·0	5·0	2·0		23·0				
Wood	6 160 ,, ,,	50·0	6·0	1·0		43·0				
Liquid fuels										
Light fuel oil	18 000 ,, ,,	86·2	12·4		1·4					
Heavy fuel oil	17 800 ,, ,,	86·1	11·8		2·1					
Distilled diesel oil (gas oil)	18 560 ,, ,,	86·3	12·8		0·9					
Kerosene	18 760 ,, ,,	86·3	13·6		0·08					
Tractor vaporizing oil	18 760 ,, ,,	86·2	13·8		0·01					
Aviation petrol	18 920 ,, ,,	85·1	14·9		0·01					
Heptane C_7H_{16}	19 280 ,, ,,	83·9	16·1							
Gaseous fuels										
Producer gas	119·6 B.Th.U./ft³		12·0	54·5			7·0	26·0	0·5	
Blue water gas	269·9 ,, ,,		49·0	4·5			4·7	41·0	0·8	
Blast furnace gas	91·3 ,, ,,		2·0	60·0			11·0	27·0		
Coal gas	426·4 ,, ,,		49·4	6·2		0·4	4·0	18·0	20·0	2·0

Typical Thermochemical Calculations. The following examples will illustrate the methods employed in thermochemical calculations.

Example 1. Calculate the heat of formation of liquid carbon disulphide from the following data.

$$C\,(s) + O_2\,(g) = CO_2\,(g) + 94\,450 \text{ cal.}$$
$$S\,(s) + O_2\,(g) = SO_2\,(g) + 70\,920 \text{ cal.}$$
$$CS_2\,(l) + 3O_2\,(g) = CO_2\,(g) + 2\,SO_2\,(g) + 251\,690 \text{ cal.}$$

Method. Underneath the molecular formula for each substance write the intrinsic energy, remembering that these values are those of the respective heats of formation with the signs reversed, whilst the intrinsic energies of elements are written as zero. If x represents the heat of formation of CS_2, then $-x$ indicates its intrinsic energy.

$$CS_2\,(l) + 3O_2\,(g) = CO_2\,(g) + 2SO_2\,(g) + 251\,690 \text{ cal.}$$
$$-x + 0 = 94\,450 + 2(-70\,920) + 251\,690$$

That is,
$$-x + 0 = -94\,450 - 141\,840 + 251\,690$$

Therefore, solving for x—

$$-x = +15\,400 \text{ cal.}$$

and
$$x = -15\,400 \text{ cal.}$$

The heat of formation of liquid carbon disulphide is, therefore, — 15 400 calories, which, being negative in sign, indicates that this compound is an endothermic compound.

Example 2. Calculate the heat of formation of hydrogen sulphide given the following data.

$$2H_2\,(g) + O_2\,(g) = 2H_2O\,(l) + 13\,740 \text{ cal.}$$
$$S\,(s) + O_2\,(g) = SO_2\,(g) + 70\,920 \text{ cal.}$$
$$2H_2S\,(g) + 3O_2\,(g) = 2SO_2\,(g) + 2H_2O\,(l) + 267\,980 \text{ cal.}$$

Method. If x represents the heat of formation of hydrogen sulphide, then its intrinsic energy is represented by $-x$. Introducing the respective intrinsic energies and solving for x—

$$2H_2S\,(g) + 3O_2\,(g) = 2SO_2\,(g) + 2H_2O\,(l) + 267\,980 \text{ cal.}$$
$$-2x + 0 = 2(-70\,920) + (-13\,740) + 267\,980$$
$$-2x = -10\,600 \text{ cal.}$$

and
$$x = +5\,300 \text{ cal.}$$

Therefore, the heat of formation of hydrogen sulphide is + 5 300 cal. and this substance is thus an exothermic compound.

Effect of Variation of Temperature on Heat of Reaction

It is often important to be able to calculate what values the heat of a reaction or the calorific value would have at temperatures other than at atmospheric temperature. For this purpose use may be made of Kirchhoff's equation (1858) in which the rate of variation of the heat of a reaction or the calorific value is related to the specific heats of the substances concerned.

Kirchhoff's equation, which is derived from the Law of Conservation of Energy, may be regarded as an application of Hess's Law; its general application is illustrated as follows.

If a process is capable of being carried out in two different ways, both starting with the same initial systems and ending with the same final systems, then with such conditions obtaining in both these processes, the increases in the heat of reaction will be identical.

Suppose first, that the reaction is conducted between the reactants at the temperature T_1 to produce the products at the same temperature, this process being associated with the absorption of heat, ΔH_1. The temperature of the products is then raised to temperature T_2 whereby a quantity of heat equal to $C_2(T_2 - T_1)$ is absorbed, C_2 being the specific heat of the reactants. The total quantity of heat absorbed by the reaction proceeding according to this first route is, $\Delta H_1 + C_2(T_2 - T_1)$.

In the second process, however, the temperature of the reactants is first raised to temperature T_2 whereby an amount of heat equivalent to $C_1(T_2 - T_1)$ is absorbed, C_1 being the specific heat of the reactants. Whilst at this temperature the reaction is allowed to proceed and an absorption of heat equivalent to ΔH_2 takes place. The total quantity of heat associated with this second process is thus $C_1(T_2 - T_1) + \Delta H_2$.

As stated above, the heat absorbed by these two processes must be identical, therefore—

$$\Delta H_1 + C_2(T_2 - T_1) = C_1(T_2 - T_1) + \Delta H_2$$

From which,

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_2 - C_1$$

Or, in more general terms—

$$\frac{dH}{dT} = \Sigma C_2 - \Sigma C_1$$

where ΣC_2 and ΣC_1 are the sums of the specific heats of the reactants and the products respectively.

Expressed in words, the increase of the heat of reaction per degree rise of temperature is equal to the sum of the specific heats of the products less the sum of the specific heats of the reactants. This may be illustrated by the following example.

Suppose it is desired to calculate the latent heat of fusion of ice at $-5°C$, given that the value of this property at $0°C$ is -80 cal./g, and that the specific heats of water and ice are 1·0 and 0·5 respectively; then—

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_2 - C_1$$

On introducing the given values,

$$\frac{-80 - \Delta H_1}{-5} = 1{\cdot}0 - 0{\cdot}5$$

Therefore, $\Delta H_1 = 77{\cdot}5$ cal.

So that the latent heat of fusion of ice at $-5°C$ is $-77{\cdot}5$ cal./g.

CHAPTER 11

REACTION VELOCITY AND CHEMICAL EQUILIBRIUM

THAT different chemical reactions proceed at different rates is well known. It will be recalled that all ionic reactions as typified by the neutralization of an acid by an alkali, or the precipitation of barium sulphate from barium chloride solution by the addition of sodium sulphate, take place almost spontaneously; whilst other reactions such as those involved during the formation of "patina" (the green scale of basic salts formed on the surface of copper when this metal is exposed to the atmosphere), or the rusting of iron, take place at an exceedingly slow rate. Yet other reactions such as the action of sulphuric acid on metallic zinc, the hydrolysis of an ester, or the oxidation of carbon at elevated temperatures, occur at such rates that the corresponding reaction is completed in a matter of minutes, or in some cases, hours.

In spite of the diverse nature of such reactions, in particular their differing velocities, certain relationships exist between the reaction velocities on the one hand, and the reaction conditions on the other.

In discussing chemical reactions it is often convenient to make a distinction between (*a*) homogeneous reactions, and (*b*) heterogeneous reactions. In homogeneous reactions the reactants and the products present in the system are all of the same type—that is, either all gases, or substances in solution; whereas the characteristic feature of heterogeneous reactions is the presence in one and the same system of phases of differing types.

THE VELOCITY OF CHEMICAL REACTION

The velocity of a chemical reaction is defined as the decrease in unit time of the concentration (in gramme molecules per litre) of one of the reactants. Homogeneous reactions take place in homogeneous systems, and heterogeneous reactions take place in heterogeneous systems.

Factors Affecting Reaction Velocity

There are four factors which affect the velocity of a chemical reaction; they are the physical nature of the reactants, the molecular concentration of the reactants, temperature, and presence of catalysts.

Physical Nature of the Reactants. Subdivision of the reactants often increases the reaction rate. Reactions often occur more rapidly in solution since in such cases subdivision has been continued down to the molecular and/or the ionic levels.

Influence of the Molecular Concentration of the Reactants. It is well known that a given weight of a metal (e.g. magnesium) will dissolve much more rapidly in concentrated hydrochloric acid than in dilute hydrochloric acid. It is important to appreciate, however, that the reaction velocity begins to diminish as soon as the reaction commences, simply because the concentrations of both hydrochloric acid and magnesium become progressively smaller with the passage of time. These generally observed facts are co-ordinated in the statement known as the *Law of Mass Action*, as proposed by Guldberg and Waage (1867) namely, that *the velocity of a chemical reaction is proportional to the active masses of the reacting substances.* By the term "active mass" is meant molecular concentration or the number of gramme molecules per unit volume. As far as gaseous systems or dilute solutions are concerned, "active mass" is given with sufficient accuracy as being equivalent to the concentration of the substance in gramme molecules per litre raised to the power of the number of molecules of that substance shown to react by the chemical equation describing the reaction involved. Thus, if in V litres of the system there are a gramme molecules of the substance A, and b gramme molecules of the substance B, which react as follows—

$$xA + yB = \text{Products of the reaction} \quad . \quad . \quad . \quad (1)$$

then, the velocity of the reaction, v, is given by the expression—

$$v = k \left(\frac{a}{V}\right)^x \left(\frac{b}{V}\right)^y \quad . \quad . \quad . \quad . \quad (2)$$

where k = the "velocity constant" of the reaction.

The velocity constant is affected in magnitude not only by the active mass, but also by the temperature, the presence of catalysts, and the physical nature of the reactants.

It is convenient to symbolize the gramme molecular concentration of a substance by writing the chemical formula of that substance within square brackets; thus, equation (2) becomes—

$$v = k\,[A]^x\,[B]^y \quad . \quad . \quad . \quad . \quad (3)$$

Influence of Temperature. No simple relationship exists connecting variation of temperature with variation in the rate of a chemical reaction. It is well known, however, that the higher the temperature, the greater the reaction velocity, and in general, an increase of 10°C may be said in many cases to double the reaction velocity. The specific variation of reaction velocity caused by temperature rise is, of course, characteristic for each reaction.

Influence of Catalysts. A *catalyst* is a substance which, when added to other substances, increases their reaction rate without itself suffering any

permanent chemical change. Catalytic action or catalysis is very common and often of profound industrial importance. For example potassium chlorate will decompose readily at 400°C, yielding potassium chloride and oxygen, but if previously mixed with a little manganese dioxide, decomposition occurs at a much lower temperature. Many other oxides, such as ferric oxide and cupric oxide, will act in a similar manner to manganese dioxide, but less effectively.

Catalytic reactions are notable for the following characteristics—

(i) The chemical composition of the catalyst remains unchanged at the end of the reaction. It should be noted that the physical state of the catalyst is often changed; if coarse granular manganese dioxide is employed to catalyze the decomposition of potassium chlorate, it will be found that a fine powder remains at the end of the reaction. Similarly, bright metallic platinum used to catalyze the reaction between oxygen and hydrogen becomes coated with a very fine film of the powder known as "platinum black."

(ii) A very small quantity of catalyst is capable of affecting a large quantity of reacting substance. Perfectly dry hydrogen chloride and ammonia are incapable of reacting, but the presence of a trace of moisture permits immediate reaction to form dense white fumes of ammonium chloride.

(iii) When a system is composed of two reversible or opposing reactions, the velocity of both reactions is affected to the same extent by a catalyst. In other words, the position of equilibrium in a reversible reaction is unaffected by the presence of a catalyst. A catalyst does not affect the yield, but only the rate at which the yield is obtained.

It is convenient to divide catalytic reactions into two groups, namely homogeneous catalysis and heterogeneous catalysis. In homogeneous catalysis the catalyst is distributed uniformly throughout the system. Examples of homogeneous catalysis are provided by the action of moisture on the interaction of hydrogen chloride and ammonia, and also the action of nitrogen peroxide to accelerate the reaction of sulphur dioxide, water vapour and oxygen in the *Lead Chamber Process* for the manufacture of sulphuric acid (*see* p. 751). In heterogeneous catalysis, the catalyst is not uniformly distributed throughout the system; most commonly the catalyst is a solid phase, whilst the reactants exist either in the liquid or the gaseous states. In the *Contact Process* (*see* p. 755) for the manufacture of sulphuric acid, the sulphur dioxide and oxygen are passed over finely divided platinum maintained at about 400°C—

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

Similarly, in the *Haber Process* (*see* p. 634) for synthesizing ammonia, hydrogen and nitrogen are passed over finely divided iron or molybdenum

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

And in *Deacon's Process* (*see* p. 788) for the manufacture of chlorine, hydrogen chloride and oxygen are passed over a catalyst of cupric chloride on hot pumice—

$$4HCl + O_2 = 2H_2O + 2Cl_2$$

The oxidation of ammonia to nitric oxide and water is extremely interesting in that it is facilitated by using as catalyst either platinum or copper, the products differing according to the catalysts employed. With platinum, nitric oxide and water result, whilst with copper, nitrogen and water are obtained.

$4NH_3 + 5O_2 = 4NO + 6H_2O$ at 500°C, platinum catalyst.

$4NH_3 + 3O_2 = 2N_2 + 6H_2O$ at 500°C, copper catalyst.

As far as gas reactions are concerned it would appear that in heterogeneous catalysis it is possible for the reactants to form a very thin "condensed" layer of gas a molecule or two thick on the metal catalyst. By this process of *adsorption* the reacting gases are brought into intimate contact so that they react the more readily to form the product or products which then evaporate from the surface.

Negative Catalysts. All the catalysts described so far may be termed positive catalysts in that they increase the velocity of a chemical reaction. There are, however, substances known as *negative catalysts* which are capable of retarding chemical reactions. One of the best examples of a negative catalyst is lead tetraethyl which is often added to petrol in order to prevent "knocking" (or "pinking"), that is, pre-ignition of the petrol vapour-air mixture on being compressed in the cylinder of an internal combustion engine just previous to sparking. Another example of negative catalysis is provided by the addition of hydroquinone to benzaldehyde to prevent the oxidation of the latter substance.

Catalyst Poisons (or Anticatalysts). Heterogeneous catalysts are very susceptible to poisoning by the adsorption of substances known as catalyst poisons. Thus, in the Contact Process for the manufacture of sulphuric acid (*see* p. 755) the sulphur dioxide and oxygen must be carefully purified to remove arsenic since this element will "poison" the platinum catalyst. In a similar manner, colloidal platinum which catalyzes the decomposition of hydrogen peroxide is poisoned by traces of hydrogen sulphide, hydrogen cyanide, mercuric chloride, carbon monoxide and hydrogen chloride.

Catalyst Promoters (or Stimulants). In contrast to catalyst poisons there are certain substances which activate solid catalysts; such activating agents are termed catalyst promoters or stimulants. For example, molybdenum is used as a promoter to the iron employed as a catalyst in the Haber Process.

CHEMICAL EQUILIBRIUM

Assuming that temperature and pressure remain constant, a system is said to be in a condition of equilibrium when there is no variation in the distribution of substances in the various parts of the system. The equilibrium is termed *stable* if it remains unchanged by slight variation in any one of the imposed conditions, whilst the equilibrium is termed *unstable* if a slight change in any one of the imposed conditions gives rise to a pronounced modification of the system. In a study of equilibria it is conventional to distinguish between homogeneous systems and heterogeneous systems.

The Law of Mass Action and Chemical Equilibria in Homogeneous Systems

In homogeneous systems all the reactants and products are phases of the same type. Chemical equilibria in such systems may be studied by the help of the Law of Mass Action. Considering the following reversible equation—

$$xA + yB \rightleftharpoons mC + nD \quad . \quad . \quad . \quad (4)$$

as previously explained, the velocity of a homogeneous reaction is proportional to the molecular concentration of the reactants, so that as the reaction proceeds the concentrations of the reactants diminish, and therefore the velocity of the forward reaction is diminished. On the other hand, in a reversible reaction the products are capable of reacting to re-form the reactants. At first the concentration of the products is very small so that this reverse or backward reaction has a very low velocity, but as the concentrations of the products increase, so the velocity of the reverse reaction shows a corresponding increase. Ultimately the velocities of the forward and backward reactions are equal and there is no resultant change in the concentrations of either reactants or of products and the system is said to be in a condition of dynamic equilibrium.

If the velocity of the forward reaction,

$$v_1 = k_1[A]^x[B]^y \quad . \quad . \quad . \quad . \quad (5)$$

and the velocity of the backward reaction,

$$v_2 = k_2[C]^m[D]^n \quad . \quad . \quad . \quad . \quad (6)$$

then, at the equilibrium condition when $v_1 = v_2$,

$$k_1[A]^x[B]^y = k_2[C]^m[D]^n \quad . \quad . \quad . \quad (7)$$

therefore

$$K = \frac{k_1}{k_2} = \frac{[C]^m[D]^n}{[A]^x[B]^y} \quad . \quad . \quad . \quad . \quad (8)$$

the ratio of the two velocity constants, k_1/k_2, being known as the equilibrium constant, K.

Since the partial pressure of a gas in a gaseous mixture is proportional to its volume, and since from Avogadro's hypothesis the volume of a gas in a gaseous mixture is proportional to its molecular concentration, it follows that the partial pressure of a gas is proportional to its molecular concentration. For the general reaction—

$$xA + yB \rightleftharpoons mC + nD$$

the condition of equilibrium at any specified temperature is

$$\frac{{p_C}^m \times {p_D}^n}{{p_A}^x \times {p_B}^y} = K_p \quad . \quad . \quad . \quad . \quad (9)$$

where ${p_C}^m$, ${p_D}^n$, ${p_A}^x$ and ${p_B}^y$ designate respectively the partial pressures at the equilibrium concentrations of the substances C, D, A and B respectively. Although partial pressures are often expressed in terms of atmospheres this is not always the case and it should be noted that the numerical value of K_p depends upon the particular units employed.

When the concentrations are expressed in terms of molal concentrations (e.g. gramme molecules per litre) the equilibrium constant is designated by K_c. Expressed in words, equations (8) and (9) may be stated as follows—

> At equilibrium the product of the molecular concentrations (or the partial pressures in the case of gaseous substances) of the substances on the right-hand side of a chemical equation, divided by the product of the molecular concentrations (or the partial pressures in the case of gaseous substances) of the substances on the left-hand side of the equation is a constant, being known as the equilibrium constant.

It should be noted that the reciprocals of the equations (8) and (9) are also constants, but by convention the equilibrium constant is expressed by placing the concentrations of the products of a chemical reaction in the numerator of the expression.

In any given system the forward and backward reactions proceed at ever-decreasing rates as equilibrium is approached, in some systems the rates of reaction are extremely slow. In this connexion it is important to emphasize that equilibrium expressions do not apply to systems which are not in a state of equilibrium. One method of ensuring that equilibrium has been attained consists in heating up one system to the temperature at which investigations are under consideration, and in cooling another system to this same temperature after being maintained for an adequate time at a higher temperature; if different relationships are found to exist in the two systems when brought to the same temperature then a longer time must be allowed, or alternatively a means must be employed to accelerate the reaction.

Influence of Temperature and Pressure on Chemical Equilibria

The influence of changes of conditions on chemical equilibria may be predicted in a qualitative manner by means of the principle of mobile equilibrium known as the Le Chatelier-Braun Principle (sometimes termed simply the Le Chatelier Principle) which may be expressed thus—

> If a change occurs in one of the factors, such as temperature or pressure, under which a system is in equilibrium, the system will tend to adjust itself so as to annul, as far as possible, the effect of that change.

Influence of Temperature Variation on the Position of Equilibrium. A consideration of the reversible reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22\,000 \text{ cal.} \quad . \quad . \quad (10)$$

in conjunction with the Le Chatelier-Braun Principle indicates that in this exothermic reaction the raising of the temperature gives rise to adjustment within the system to drive down the temperature. This is effected by dissociation of some of the ammonia into nitrogen and hydrogen which, being an endothermic reaction, absorbs heat. Thus, in exothermic reactions the raising of the reaction temperature displaces the equilibrium towards the left, so that a lower product yield is obtained. In the specific case of ammonia quoted above, if maximum conversion of nitrogen and hydrogen to ammonia is to be effected it is clearly desirable that the reaction temperature must be as low as is compatible with a reasonable reaction rate.

In an endothermic reaction the increasing of the reaction temperature gives rise to an increase in the equilibrium concentration of the products. Thus, in the endothermic reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43\,200 \text{ cal.} \quad . \quad . \quad (11)$$

the yield increases as the temperature rises.

The Le Chatelier-Braun Principle thus only permits of a qualitative indication of the direction in which equilibrium will be displaced by variation in reaction temperature. The effect of temperature variation upon the equilibrium constant K of a balanced chemical reaction was shown by van't Hoff to be as follows—

$$\frac{d \log K}{dT} = \frac{Q_v}{RT^2} \quad . \quad . \quad . \quad . \quad (12)$$

where K = equilibrium constant, T = absolute temperature, Q_v = heat of reaction at constant volume, and R = gas constant. This expression is known as the van't Hoff isochore. Assuming that Q_v, the heat of reaction, is independent over a small range of temperature, this expression may be integrated thus—

$$\log_{10} K_2 - \log_{10} K_1 = \frac{-Q_v}{4{\cdot}576}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad . \quad . \quad (13)$$

where K_1 and K_2 are the equilibrium constants of the reaction at absolute temperatures T_1 and T_2 respectively and Q_v is the heat of reaction expressed in gramme calories absorbed at constant volume.

Influence of Pressure Variation on the Position of Equilibrium. In considering the influence of pressure variation on the position of equilibrium in gaseous systems it is necessary to distinguish between those systems in which the number of molecules remains unchanged after the reaction has occurred, and those systems in which different numbers of molecules appear on the two sides of the chemical equation.

Equilibria in Gaseous Systems where the Number of Molecules remains unchanged. A familiar example of this type of gaseous reversible systems is provided by the reaction—

$$\underset{2x}{2HI(g)} \rightleftharpoons \underset{(a-x)}{H_2(g)} + \underset{(b-x)}{I_2(g)} \quad . \quad . \quad . \quad . \quad (14)$$

Consider that the initial volume of the system is V litres, the initial amount of hydrogen is a gramme molecules and that of iodine b gramme molecules, and that when equilibrium is attained there have been formed $2x$ gramme molecules of hydrogen iodide; these concentrations are included below equation (14), above. The equilibrium concentrations of hydrogen, iodine and hydrogen iodide are therefore $(a - x)/V$, $(b - x)/V$ and $2x/V$ gramme molecules/litre respectively. Applying the Law of Mass Action to equation (14)—

$$K_c = \frac{[H_2]\,[I_2]}{[HI]^2} \quad . \quad . \quad . \quad . \quad (15)$$

and substituting values in this expression—

$$K_c = \frac{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}{\left(\frac{2x}{V}\right)^2} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$K_c = \frac{(a-x)\,(b-x)}{4x^2} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

whence $2x$, the number of gramme molecules of hydrogen iodide at equilibrium, is given by—

$$2x = \frac{a + b - \sqrt{a^2 + b^2 - ab(2 - 16K_c)}}{1 - 4K_c} \quad . \quad . \quad (18)$$

It should be noted that the term V cancels out both from the numerator and denominator; it follows therefore that this particular equilibrium is not affected by changes in the volume occupied by the reacting gases, this reaction being thus *independent of the pressure*. This statement is true for

any homogeneous reaction in which the number of molecules on each side of the chemical equation is the same.

Equilibria in Gaseous Systems where the Number of Molecules is changed. In accord with the Le Chatelier-Braun Principle, increase in pressure within a system favours those reactions giving rise to a decrease in volume. This is illustrated by the case of the dissociation of phosphorus pentachloride. If initially there are a gramme molecules of phosphorus pentachloride contained in a volume of, say, V litres, and that resulting from dissociation there are formed b gramme molecules of phosphorus trichloride, it follows from the equation that there must also be formed b gramme molecules of chlorine.

$$\underset{(a-b)}{PCl_5(g)} \rightleftharpoons \underset{b}{PCl_3(g)} + \underset{b}{Cl_2(g)} \quad . \quad . \quad . \quad (19)$$

At equilibrium therefore the molecular concentration of phosphorus pentachloride will be $(a - b)/V$ gramme molecules per litre, whilst those of phosphorus trichloride and chlorine are both b/V gramme molecules per litre. On application of the Law of Mass Action, the value of the equilibrium constant is as follows—

$$K = \left(\frac{b}{V}\right)^2 \Big/ \left(\frac{a-b}{V}\right)$$

$$= \frac{b^2}{(a-b)V} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

If the equilibrium constant K is to remain of constant numerical value, it follows, since the term V occurs only in the denominator of equation (20), that with increase in the value of V the greater must be the numerical value of the expression $b^2/(a - b)$; in other words, the greater the amount of dissociation b. Expressed in another way, reduction of pressure (without removing some of the reactants from the system) gives rise to an increase in the dissociation and conversely. Expressed in yet another way, decrease in pressure moves the position of equilibrium in the direction of increase in the number of molecules, that is, it favours dissociation.

Influence on the Position of Equilibrium of Adding One of the Products of the Reaction. Referring again to the thermal dissociation of phosphorus pentachloride,

$$\underset{(a-b)}{PCl_5(g)} \rightleftharpoons \underset{b}{PCl_3(g)} + \underset{b}{Cl_2(g)}$$

Assuming that at equilibrium there are $(a - b)$ gramme molecules of phosphorus pentachloride and b gramme molecules of phosphorus trichloride and b gramme molecules of chlorine, and that the volume occupied by the system is V litres. From the Law of Mass Action it has been established that $K = b^2/(a - b)V$. If to this system in equilibrium c gramme

molecules of chlorine are then introduced, the volume of the system being maintained constant, then the concentration of chlorine will be increased to $(b + c)$ gramme molecules. In order that the numerical value of K shall remain constant the concentration of phosphorus trichloride must decrease and that of phosphorus pentachloride must increase. In other words, the dissociation will be retarded. In a similar manner the introduction of a high concentration of phosphorus trichloride into the system prevents the dissociation of phosphorus pentachloride.

The physico-chemical principles discussed above apply equally to the system—

$$3KCNS + FeCl_3 \rightleftharpoons Fe(CNS)_3 + 3KCl \quad . \quad . \quad (21)$$

The application of the Law of Mass Action to this system gives the equilibrium constant as follows—

$$K = \frac{[Fe(CNS)_3]\,[KCl]^3}{[FeCl_3]\,[KCNS]^3} \quad . \quad . \quad . \quad . \quad (22)$$

The addition of a saturated aqueous solution of potassium chloride causes a pronounced reduction in the intensity of the red colouration due to the ferric thiocyanate since there must be a reduction in the value of the molecular concentration of ferric thiocyanate in the numerator of equation (22) if the numerical value of K is to remain constant. Likewise, the addition of either ferric chloride or of potassium thiocyanate to the system leads to an intensification of the red colouration since the numerical value of the numerator must increase if the equilibrium constant K is to be maintained at a constant value.

The following typical examples of chemical equilibria in homogeneous systems illustrate the importance of the factors discussed above. In examples (i), (ii) and (iii) the total number of molecules remains unchanged, whereas a change in the total number of molecules is involved in examples (iv) to (vii).

(i) *The Synthesis of Nitric Oxide* (*Birkeland-Eyde Process*). The reaction involved in this synthesis is as follows—

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43\,200 \text{ cal.}$$

It will be noted from the equation that there are two molecules on each side of the equation; variation in pressure therefore does not affect the concentration of nitric oxide at equilibrium.

On the other hand since the reaction is endothermic in nature, rise in reaction temperature gives rise to an increase in the yield of nitric oxide. Under actual working conditions the high temperatures necessary in the Birkeland-Eyde process are obtained by using an electric arc; the following data illustrates the variation of yield of nitric oxide with varying temperature.

TABLE 40

Synthesis of Nitric Oxide

Temperature (°C)	Equilibrium Percentage of Nitric Oxide
1811	0·37
2033	0·64
2195	0·997
3000	4·5
3200	5·0

In actual practice the yield of nitric oxide never exceeds approximately 2 per cent, since although the arc temperature is in excess of 3000°C, the gases pass rapidly through regions at a lower temperature so that the proportion of nitric oxide in the final gaseous mixture tends to correspond to the equilibrium composition at these lower temperatures. In actual fact, however, the gas velocity attained in practice is so high that very rapid cooling occurs and the new equilibrium corresponding to lower contents of nitric oxide has insufficient time to be attained.

(ii) *The Synthesis of Hydrogen Iodide.* The synthesis and the thermal dissociation of hydrogen iodide has been studied by Bodenstein and his co-workers, whose results are given below in Table 41.

TABLE 41

The Reaction $H_2 + I_2 \rightleftharpoons 2HI$ *at* 444°C

Relative Partial Pressures						
Initial		Equilibrium			K_p	p_{HI} (calc.)
H_2	I_2	H_2	I_2	HI		
8·10	2·94	5·27	0·13	5·66	47	5·3
7·94	5·30	3·18	0·54	9·52	52	9·3
8·07	9·17	1·40	2·60	13·34	49	13·4
8·12	14·44	0·72	7·03	14·82	43	14·7

Note: The partial pressures are relative values but this fact does not affect the value of K_p.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) - 11\,820 \text{ cal.} \quad . \quad . \quad (23)$$

Table 41 shows that with various proportions of the two reactants hydrogen and iodine the equilibrium constant, K, has a numerical value of approximately 48 at 444°C. The values of p_{HI} (calc.) given in column seven of Table 41 are obtained by introducing the value of K_p (48 in this case) along with known values for the initial pressures of hydrogen and iodine (equivalent to a and b in equation (18)) and evaluating for $2x$. It should be noted that these calculated values for $2x$ as given in column seven are in fair agreement with the observed pressures as given in column five.

(iii) "*The Water-gas*" *Reaction.* This reversible reaction is of considerable importance in industry. In equation form this reaction may be depicted as follows—

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad . \quad . \quad (24)$$

The equilibrium constant is—

$$K_p = \frac{p_{CO} \times p_{H_2O}}{p_{CO} \times p_{H_2}} \quad . \quad . \quad . \quad . \quad (25)$$

partial pressures being employed for the sake of convenience. From previous discussion it will be clear that this reaction is independent of pressure. The reaction is however endothermic in character, so that as the temperature rises the yields of carbon monoxide and water should increase; in other words, the numerical value of the equilibrium constant should increase with rising temperature. Typical values for K_p at various temperatures are given in Table 42.

TABLE 42

Variation with Temperature of the Equilibrium Constant for the "Water Gas" Reaction

Temperature (°C)	K_p
686	0·534
786	0·840
886	1·197
1005	1·620
1255	2·68
1324	2·93
1495	3·83

It is usually desirable in industrial practice to obtain a high yield of hydrogen from this reaction, and this is effected by maintaining the temperature

at as low a point as possible. In addition, with the object of reducing the content of carbon monoxide in the gaseous mixture it is usual to employ an excess of steam.

(iv) *The Synthesis of Ammonia* (*Haber Process*). The exothermic synthesis of ammonia from its component elements nitrogen and hydrogen is of considerable technical importance.

$$\underset{\text{1 vol}}{N_2(g)} + \underset{\text{3 vols}}{3H_2(g)} \rightleftharpoons \underset{\text{2 vols}}{2NH_3(g)} + 22\,000 \text{ cal.} \quad . \quad . \quad (10)$$

From equation (10) it follows in the light of previous discussion that increase in pressure should favour moving the position of equilibrium in the direction of a decrease in the number of molecules—that is, it should favour the formation of ammonia. On the other hand, since the reaction is exothermic in nature, increase in reaction temperature leads to a reduction in the yield of ammonia. Thus, in order to obtain the maximum conversion of nitrogen and hydrogen to ammonia it is essential to work at as low a temperature as is consistent with a reasonable reaction rate; normally a working temperature of approximately 500°C is employed; in addition it is usual to employ a catalyst with the object of accelerating the synthesis. Values for the equilibrium percentage of ammonia at differing temperatures and pressures are given in Table 43.

TABLE 43

The $N_2 + 3H_2 \rightleftharpoons 2NH_3$ *Equilibrium*

Temperature (°C)	Equilibrium Percentage of Ammonia (Volume percentage at pressures of)			
	1 atmos.	100 atmos.	200 atmos.	1000 atmos.
200	15·33	80 6	85·8	98·3
300	2·18	52·1	62·8	92·6
400	0·44	25·1	36·8	79·8
500	0·129	10·4	17·6	57·5
600	0·049	4·47	8·25	31·4
700	0·022	2·14	4·11	12·9
800	0·012	1·15	2·24	
900	0·007	0·68	1·34	
1000	0·004	0·44	0·87	

The maximum conversion of nitrogen and hydrogen to ammonia occurs when approximately stoichiometric proportions are employed.

Effect of Pressure on Ammonia Synthesis. Suppose that initially there

are present 1 mole of nitrogen and 3 moles of hydrogen, and that x moles of nitrogen are converted into ammonia.

$$\underset{(1-x)}{N_2(g)} + \underset{3(1-x)}{3H_2(g)} \rightleftharpoons \underset{2x}{2NH_3(g)} + 22\,000 \text{ cal.}$$

At equilibrium therefore there will also be present $3(1 - x)$ moles of hydrogen along with $2x$ moles of ammonia. The total number of moles present at equilibrium is therefore—

$$= (1 - x) + 3(1 - x) + 2x$$
$$= 4 - 2x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Since the partial pressure of any particular molecule is proportional to the concentration of that molecule in a gaseous mixture, it follows that if the total pressure is represented by P, then the equilibrium constant, K_p, may be evaluated thus—

$$K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

$$= \frac{\left(\frac{2x}{4-2x}\right)^2 P^2}{\frac{(1-x)P}{4-2x} \times \left(\frac{3(1-x)P}{4-2x}\right)^3}$$

$$= \frac{16x^2(2-x)^2}{27P^2(1-x)^4} \quad . \quad . \quad . \quad . \quad . \quad (28)$$

If x, the fraction of nitrogen converted to ammonia, is small, then equation (28) may be simplified thus—

$$K_p = \frac{64x^2}{27P^2}$$

or,

$$x^2 = \frac{27}{64} K_p P^2 \quad . \quad . \quad . \quad . \quad (29)$$

In other words, under these latter conditions the fraction of nitrogen converted to ammonia is directly proportional to the total pressure P. It should be noted that this statement is in accord with the result to be expected from the Le Chatelier-Braun Principle, in that increase in pressure should tend to move the position of equilibrium in the direction of a decrease in the number of molecules. It should also be noted from Table 43 that at the higher temperatures the equilibrium percentage of ammonia at 200 atmospheres is approximately twice that at 100 atmospheres.

(v) *The Synthesis of Sulphur Trioxide* (*Contact Process*). The formation of sulphur trioxide by the exothermic reversible reaction between sulphur

dioxide and oxygen serves as another illustration of the application of the Law of Mass Action. This reaction is of great importance as an industrial method for the manufacture of sulphuric acid (*see* p. 755). The equation for this reaction is as follows—

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) + 93\,900 \text{ cal.} \quad . \quad . \quad (30)$$

The application of the Law of Mass Action to this reaction gives for the equilibrium constant K_p—

$$K_p = \frac{p_{SO_3}}{p_{SO_2} \times p_{O_2}^{\frac{1}{2}}} = \frac{p_{SO_3}}{p_{SO_2} \times \sqrt{p_{O_2}}} \quad . \quad . \quad . \quad (31)$$

Since this reaction is exothermic in nature the yield of sulphur trioxide will decrease with an increase in the reaction temperature; in other words, the numerical value for the equilibrium constant will decrease with rising temperature; this is illustrated by the data given in Table 44.

TABLE 44

Variation of K_p with Temperature for the Reaction

$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$

Temperature (°C)	528	579	627	680	727	789	832	897
K_p	31·3	13·8	5·54	3·24	1·86	0·96	0·68	0·36

In order that as large a yield of sulphur trioxide as possible may be obtained, the numerical value of K_p should obviously be as large as possible; in other words, the operating temperature should be as low as possible. However, since under these conditions the reaction rate is very slow it is customary to employ a catalyst to accelerate the reaction and permit of equilibrium conditions being obtained more rapidly. By this means a moderate temperature of approximately 450°C may be employed. Although increase in pressure gives rise to an increase in the yield of sulphur trioxide the effect is not great so that in technical practice advantage is not taken of this fact. Using equation (31) the following important results may be deduced.

		SO_2	+	$\frac{1}{2}O_2$	$\rightleftharpoons$	SO_3
Initial amounts in molecules	=	1		$\frac{1}{2}$		0
Equilibrium amounts in molecules	=	$(1 - x)$		$\frac{1}{2}(1 - x)$		x
Total number of molecules present at equilibrium	=	$1\frac{1}{2} - \frac{1}{2}x$				
	=	$\frac{3 - x}{2}$				

Partial pressures (if P is the total pressure) $= \frac{2(1-x)P}{3-x} \quad \frac{(1-x)P}{3-x} \quad \frac{2xP}{3-x}$

Therefore, since $$K_p = \frac{p_{SO_3}}{p_{SO_2} \times \sqrt{p_{O_2}}} \quad . \quad . \quad . \quad (31)$$

On introducing partial pressures as given above $$K_p = \frac{x}{(1-x)\sqrt{\frac{1-x}{3-x}P}} \quad . \quad . \quad . \quad (32)$$

From equation (31) it may be deduced that an increase in the concentration of oxygen will increase the yield of sulphur trioxide if the numerical value of K_p is to be kept constant. On the other hand, if the yield of sulphur trioxide is already good (i.e. if the value for x is close to unity) then it will be noted from equation (32) that the partial pressure of the oxygen in the equilibrium mixture exerts an influence determined not by its concentration, but *by the square root of its concentration.*

(vi) *Dissociation of Nitrogen Tetroxide.* The dissociation of nitrogen tetroxide provides another example of gaseous equilibrium to which the Law of Mass Action may be applied.

$$\underset{(1-x)}{N_2O_4(g)} \rightleftharpoons \underset{2x}{2NO_2(g)} \quad . \quad . \quad . \quad (33)$$

Increase in pressure will decrease the degree of the dissociation. Since the dissociation reaction is endothermic in nature, increase in reaction temperature should favour dissociation; this is found to be the case, the equilibrium constant increasing in numerical value with rising temperature. If initially there is one gramme molecule of nitrogen tetroxide, and if at the equilibrium position a fraction x g.mol. is dissociated, then at this equilibrium position there will be $(1-x)$ g.mol. of nitrogen tetroxide and $2x$ g.mol. nitrogen peroxide. The total number of gramme molecules is—

$$1 - x + 2x = 1 + x \text{ g.mol.} \quad . \quad . \quad . \quad (34)$$

If the pressure within the system be maintained constant then the volume occupied by the system at the equilibrium position will be $(1+x)$ times as great as that it occupied before dissociation had occurred. Conversely, the density will be lowered by the factor $\frac{1}{1+x}$. Taking the density of nitrogen tetroxide to be 46, then the density of the equilibrium mixture is given by the following expression—

Density of equilibrium mixture $= d = \frac{46}{1+x} \quad . \quad . \quad . \quad (35)$

Hence, the degree of dissociation $= x = \frac{46-d}{d} \quad . \quad . \quad . \quad (36)$

(vii) *Dissociation of Phosphorus Pentachloride.* Using the method described above the degree of dissociation of phosphorus pentachloride may be evaluated. The reaction involved is as follows—

$$\underset{(1-x)}{PCl_5(g)} \rightleftharpoons \underset{x}{PCl_3(g)} + \underset{x}{Cl_2(g)} \quad . \quad . \quad . \quad (19)$$

Suppose that initially there was one gramme molecule of phosphorus pentachloride and that resulting from dissociation a fraction of x g.mol. dissociated. In the equilibrium mixture there will, therefore, be $(1 - x)$ g.mol. of phosphorus pentachloride, x g.mol. of phosphorus trichloride and x g.mol. of chlorine; the total number of gramme molecules present in the equilibrium mixture is thus—

$$(1 - x) + x + x$$
$$= 1 + x \text{ g.mol.} \quad . \quad . \quad . \quad . \quad (37)$$

From previous discussion in the case of nitrogen tetroxide above, it follows that if the density of PCl_5 be taken as 104·2—

$$\text{Density of equilibrium mixture} \quad = d = \frac{104{\cdot}2}{1 + x} \quad . \quad . \quad . \quad . \quad (38)$$

$$\text{Therefore the degree of dissociation } x = \frac{104{\cdot}2 - d}{d} \quad . \quad . \quad . \quad (39)$$

Equilibria in Homogeneous Liquid Systems

The Law of Mass Action is applicable not only to homogeneous gaseous systems, but also to homogeneous liquid systems. One of the best known examples of such homogeneous liquid equilibrium is provided by the reaction between ethyl alcohol and acetic acid—

$$\underset{a-x}{C_2H_5OH} + \underset{b-x}{CH_3COOH} \rightleftharpoons \underset{x}{CH_3COOC_2H_5} + \underset{c+x}{H_2O} \quad . \quad (40)$$

ethyl acetate and water being formed.

If initially there are a g.mol. of ethyl alcohol, b g.mol. of acetic acid, and c g.mol. of water all contained within a volume V, and if at equilibrium x g.mol. of ethyl acetate are formed, then the equilibrium concentrations of the four substances will be as follows—

Ethyl alcohol	$a - x/V$
Acetic acid	$b - x/V$
Ethyl acetate	x/V
Water	$c + x/V$

Applying the Law of Mass Action—

$$K = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[C_2H_5OH]\,[CH_3COOH]} = \frac{x(c + x)}{(a - x)\,(b - x)} \quad . \quad (41)$$

Starting with one gramme molecule each of the alcohol and the acid respectively and no water, it has been found that the number of gramme molecules of the ester is 0·667. Introducing these values (i.e. $a = 1$, $b = 1$, $c = 0$, $x = 0{\cdot}667$) in equation (41) above—

$$K = \frac{0{\cdot}667^2}{0{\cdot}333^2} = 4{\cdot}0 \quad . \quad . \quad . \quad . \quad (42)$$

Table 45 gives some values for the amounts of ester produced by the interaction of differing amounts of alcohol with one gramme molecule of acid. In this case $b = 1$ and $c = 0$, therefore—

$$K = 4 = \frac{x^2}{(a - x)\,(1 - x)} \quad . \quad . \quad . \quad (43)$$

On multiplying out, $3x^2 - 4(a + 1)x + 4a = 0$

Therefore $$x = \tfrac{2}{3}\left(1 + a - \sqrt{1 - a + a^2}\,\right) \quad . \quad . \quad . \quad (44)$$

The figures given in column five in Table 45 have been calculated by means of equation (44). The agreement between the observed and calculated values should be noted.

TABLE 45

The Acetic Acid—Ethyl Alcohol—Ethyl Acetate—Water Equilibrium

Initial g.mol. of		Equilibrium g.mol. of Ethyl Acetate	K	g.mol. of Ethyl Acetate
Acetic Acid	Ethyl Alcohol			
b	a	x (observed)		x (calculated)
1·0	0·18	0·171	3·9	0·171
1·0	0·33	0·293	3·3	0·301
1·0	0·50	0·414	3·4	0·423
1·0	1·00	0·667	4·0	0·667
1·0	2·00	0·858	4·6	0·850
1·0	8·00	0·966	3·9	0·970

Since this reaction proceeds without the liberation or the absorption of appreciable quantities of heat it may be deduced from the Le Chatelier-Braun Principle that the composition of the equilibrium mixture will not be affected greatly by variation in the temperature of the system. This has been verified experimentally.

The Application of the Law of Mass Action to Heterogeneous Systems

Although in the foregoing discussion the Law of Mass Action has only been applied to homogeneous systems in equilibrium, this law may also be applied to heterogeneous systems in a state of equilibrium provided that whenever a solid substance is involved in a chemical reaction its active mass is regarded as constant, irrespective of the amount of the substance present; in other words, it is assumed that the reaction involved occurs in one phase only. For example taking the well-known dissociation of calcium carbonate to illustrate the points involved—

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \quad . \quad . \quad . \quad (45)$$

Assuming that this reaction occurs in the gaseous phase and that the active masses of calcium carbonate and calcium oxide are constant—

$$K_c = \frac{[CaO]\,[CO_2]}{[CaCO_3]} \quad . \quad . \quad . \quad . \quad (46)$$

or,

$$K_p = \frac{k' \times p_{CO_2}}{k''} \quad . \quad . \quad . \quad . \quad (47)$$

where p_{CO_2} = the partial pressure of the carbon dioxide, k' = the constant active mass of calcium oxide in the gas phase, and k'' = the constant active mass of calcium carbonate in the gas phase.

Thus

$$p_{CO_2} = \frac{k''}{k'} \times K \quad . \quad . \quad . \quad . \quad . \quad (48)$$

That is

$$p_{CO_2} = \text{a constant} \quad . \quad . \quad . \quad . \quad . \quad (49)$$

The truth of this relationship is borne out by the experimental fact that at any given temperature the pressure of carbon dioxide, in equilibrium with calcium carbonate and calcium oxide, is a constant and independent of the relative amounts of these two solids. Thus, this system exists in a condition of equilibrium at any given temperature when a definite pressure of carbon dioxide exists.

Similarly in the case of the reaction—

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g) \quad . \quad . \quad . \quad (50)$$

it may be deduced that for a condition of equilibrium to exist at any given temperature the ratio p^2_{CO}/p_{CO_2} is a constant. This ratio may therefore be taken as the equilibrium constant, that is—

$$K_p = \frac{p^2_{CO}}{p_{CO_2}} \quad . \quad . \quad . \quad . \quad . \quad (51)$$

This reaction is endothermic in character and the equilibrium constant

therefore increases as the temperature rises; this is shown in the data given in Table 46.

TABLE 46

The $CO_2 + C \rightleftharpoons 2CO$ *Equilibrium*

(*after Rhead and Wheeler*)

Temperature °C	Percentage CO	Percentage CO_2	K_p
850	93·77	6·23	14·11
900	97·78	2·22	43·07
950	98·68	1·32	73·77
1000	99·41	0·59	167·5
1050	99·63	0·37	268·3
1100	99·85	0·15	664·7
1200	99·94	0·06	1665·0

It should be noted therefore that at any given temperature, equilibrium is only possible when there exists a definite pressure of carbon dioxide. This is precisely the result which is obtained by the application of the Phase Rule.

Activity of Solutes. In general, if molecular concentrations are employed to represent the active masses of the components, the Law of Mass Action cannot be applied without modification to reactions occurring in solution. This is due to the fact that in such cases the numerical value of the equilibrium constant exhibits considerable variation. With the object of obtaining agreement with the Law of Mass Action it is conventional to substitute for molecular concentrations the so-called "activities" of the various components. The relationship of activity and molecular concentration is shown by the following expression—

$$a = cf \quad . \quad . \quad . \quad . \quad . \quad (52)$$

where a = activity, c = molecular concentration, and f = activity coefficient.

The activity coefficient f is the factor by which the molecular concentration must be multiplied if the Law of Mass Action is to be obeyed.

CHAPTER 12

ELECTROCHEMISTRY

ELECTROLYTIC CONDUCTION

Electrical conductors may be divided into two well-marked classes—

(*a*) Electronic conductors, and

(*b*) Electrolytic conductors or electrolytes.

The electrical conductivity of electronic conductors is due to the presence of free electrons which serve as current carriers. A metal, a typical electronic conductor, is regarded as a three-dimensional assembly of positively-charged metal ions and the corresponding free electrons. Electronic conductors conduct electricity without suffering any permanent change.

Electrolytic conductors are distinguished from electronic conductors in that in the former the passage of an electric current is accompanied by a chemical reaction (or reactions) and the transfer of matter. An electrolyte however, although containing positive ions like a metal, also contains negative "ions" instead of free electrons as present in a metal. The positive ions present in a metallic salt are often metal atoms—but maybe radicals—which have lost one or more electrons, the number of electrons lost corresponding to the valency of the metal or the radical. The negative ions are either non-metal atoms or acid radicals which have gained one or more electrons, according to their valencies, from the metal atoms or the positive radicals.

In the solid or crystalline state most salts are composed entirely of an assembly of ions, and as such may be regarded as non-conductors from the electrical point of view. However, when such a salt is melted, or when it is dissolved in water or some other similar solvent, the rigid lattice structure breaks up, the ions gaining an independence of movement so that under the influence of a potential difference the positive ions migrate in one direction, and the negative ions in another. On account of the absence of free electrons in metallic salts, the passage of an electric current either through a fused salt, or through a solution of a salt, is due entirely to the migration of the positive and the negative ions.

The number of electric charges possessed by an ion and corresponding to its valency is indicated by writing as an index one or more positive or negative signs after the chemical symbol for the element or the radical concerned according as to whether the ion is either positive or negative in

character. Thus, Na^+ depicts the monovalent sodium ion, Cl' the monovalent chloride ion, SO_4'' the divalent sulphate ion, and Cu^{++} the divalent cupric ion. Sometimes, for ease of printing, a dot is used to indicate each positive charge, thus $Na^{\cdot}$, $Cu^{\cdot\cdot}$.

In the case of electrolytes which exhibit an ionic structure in the solid state, the solution of the salt in a suitable solvent results in the pushing apart of the ions by the molecules of the solvent and the variations in the conductivity of such electrolytes are considered to be due to variations in the "activity" of the ions, resulting from the mutual attraction of oppositely charged ions which gives rise to a modified distribution of ions in the solution. In strong solutions there exist ionic doublets formed by the tendency of oppositely charged ions to cling together in pairs. Thus although ionization may be complete, dissociation is incomplete except in very dilute solutions. Typical examples of compounds which behave in this manner include the majority of metallic salts and the metallic hydroxides—

$$K^+Cl' \rightleftharpoons K^+ + Cl'$$

$$Na^+OH' \rightleftharpoons Na^+ + OH'$$

$$Ca^{++}Cl_2 \rightleftharpoons Ca^{++} + 2Cl'$$

On the other hand, there are certain electrolytes which form real molecules in which the opposite electric charges of the ions are neutralized by one another, chemical bonds uniting the radicals of the ions. In such cases, molecules as well as ions are capable of existence in solution, particularly in strong solutions, the progressive increase in the ionization of such electrolytes with increasing dilution being due to electrolytic dissociation of the electrically neutral molecules. Such compounds, which are said to exhibit *reversible ionization*, include the acids which form real molecules capable of ionization by contact with water to form the *hydroxonium ion* H_3O^+—

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl'$$

$$H_2SO_4 + 2H_2O \rightleftharpoons 2H_3O^+ + SO_4''$$

Certain metallic salts (e.g. mercury salts) have also been shown to have a molecular structure in the solid state instead of an ionic structure.

Electrolytes may be classified according to the number and the valency of the ions produced. Thus sodium chloride and copper sulphate may both be termed *binary electrolytes* since one molecule of each of these compounds is capable of producing two ions. On the other hand, in the case of sodium chloride both the ions produced are univalent so that this compound may also be called a *uni-univalent* electrolyte. Copper sulphate however yields two bivalent ions and so is called a *bi-bivalent* electrolyte. The valencies of the ions are quoted in the order positive-negative. Calcium chloride and potassium sulphate are both *ternary electrolytes* since one molecule

of each yields three ions; the former of these compounds is *bi-univalent*, whilst the latter is *uni-bivalent*.

ELECTROLŸSIS

Electrolysis is the passage of a direct electric current through an electrolyte by way of two electrodes which are electronic conductors. The electrode connected to the positive terminal of the supply is known as the *anode*, whilst that connected to the negative terminal of the supply is known as the *cathode*.

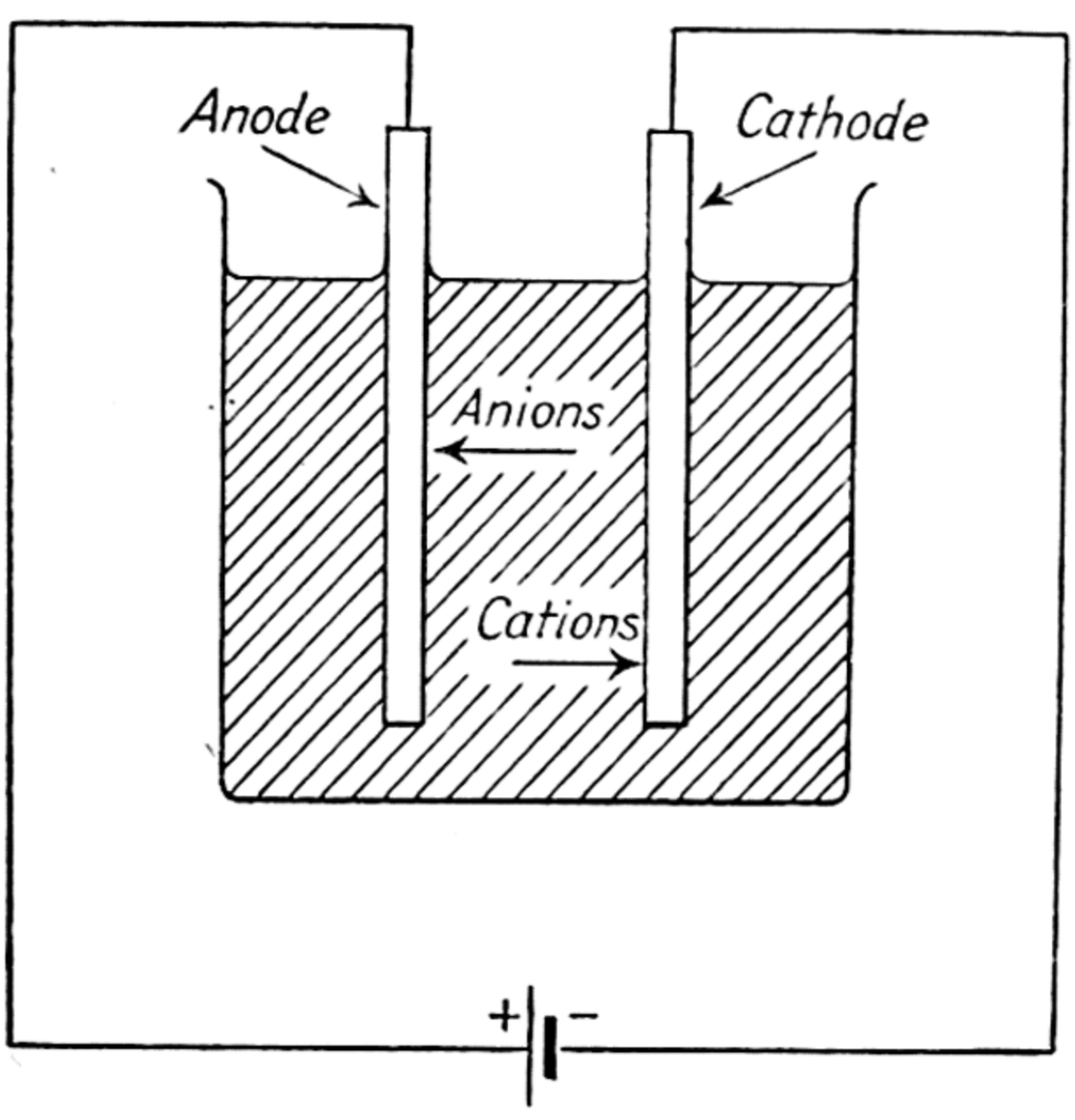


FIG. 94. Passage of Electrical Current through Electrolyte

The positively-charged ions which under a potential difference migrate to the cathode are termed *cations*; whilst those which are negatively-charged and which migrate to the anode are termed *anions* (*see* Fig. 94). When an electric current passes from an electronic conductor to an electrolyte, the transition from electrons to ions as current carriers involves the transference of electrons to or from ions, or atoms or groups of atoms at the interface of the electrolyte and the electronic conductor. These electron transfers constitute chemical changes which, as stated above, are a necessary accompaniment of the passage of electricity through an electrolyte.

The chemical reactions which take place at the surface of an anode are chemical oxidation processes, whilst those occurring at the surface of a cathode are chemical reduction processes. There are, therefore, in electrolysis two separate and distinct types of chemical reactions—the anode reaction (or reactions), and the cathode reaction (or reactions). The essential chemical character of all electrode reactions in electrolysis may be explained in terms of the gain, or the loss of electrons by ions, or atoms, or radicals at the surfaces of the electrodes, followed in certain cases by secondary processes.

On receiving electrons at the cathode the cations become atoms, or radicals as the case may be, and are discharged at the electrode surface. Similarly each anion yields electrons to the anode equal in number to its negative charge, becoming an atom or a radical in the process, and being discharged at the anode surface. Instead of being set free as atoms which may be collected in the molecular state as matter at the electrode surface, the ions on discharging at the electrode surface may give rise to

the production of primary products which may react, (*a*) with one another, (*b*) with the electrode itself, or (*c*) with the electrolyte, to give secondary products. The following examples will serve to illustrate these phenomena.

Electrolysis of Dilute Sulphuric Acid. A dilute solution of sulphuric acid contains hydrogen ions, sulphate ions and a small concentration of hydroxyl ions, OH', resulting from the electrolytic dissociation of water.

$$H_2O \rightleftharpoons H^+ + OH'$$

In an electrolyte containing a number of different ions undergoing electrolysis, the ion which is discharged first at an electrode is that having the lowest *discharge potential*, that is, the ion requiring the smallest e.m.f. for its discharge as a neutral atom or radical. The discharge potential of an ion is dependent upon the chemical composition and the physical nature of the electrode, and upon the concentration of the particular ion in the electrolyte. In the case of metals, the relative discharge potentials are in general agreement with the position of the metals in the electrochemical series; that is, the higher the position any given metal occupies in the electrochemical series, the higher the e.m.f. for its discharge at an electrode surface.

On electrolysis of dilute sulphuric acid using platinum electrodes, hydrogen ions and hydroxyl ions are discharged, the former at the cathode and the latter at the anode. Hydroxyl ions are discharged in preference to sulphate ions since the former have a lower discharge potential than sulphate ions.

The electrolysis may be represented by the following—

(*A*) *Cathode reactions*

(i) $H^+ + e = H$

(ii) $2H = H_2$

(*B*) *Anode reactions*

(i) $OH' - e = OH$

(ii) $4OH = 2H_2O + O_2$

} where e = an electron.

The progressive removal of hydroxyl ions causes more water molecules to dissociate in order to re-establish the equilibrium. The net result is the concentration of sulphuric acid in the electrolyte.

Electrolysis of Sodium Chloride Solution. An aqueous solution of sodium chloride contains sodium ions and chloride ions from the salt, and hydrogen and hydroxyl ions from the water. When electrodes of platinum or of graphite are employed hydrogen ions and not sodium ions are discharged at the cathode, the hydrogen ions having a lower discharge potential under these conditions. At the anode, chloride ions are

discharged, since they have a lower discharge potential than the hydroxyl ions. These electrode reactions are as follows—

(*A*) *Cathode reactions*

$$\text{(i)} \quad H^+ + e = H$$
$$\text{(ii)} \quad 2H = H_2$$

(*B*) *Anode reactions*

$$\text{(i)} \quad Cl' - e = Cl$$
$$\text{(ii)} \quad 2Cl = Cl_2$$

Thus, the progressive removal of hydrogen ions causes more water molecules to dissociate so that ultimately the concentration of the hydroxyl ions attains that of the sodium ions; in other words, the sodium chloride has been converted into sodium hydroxide.

If, instead of a carbon or a platinum cathode, a mercury cathode is employed, as in the Castner-Kellner cell (*see* p. 428), the discharge potential of the sodium ions is less than that of the hydrogen ions. Thus, sodium is liberated at the mercury cathode surface where it amalgamates with the mercury. This amalgam is decomposed by water in another compartment in which the amalgam constitutes an anode, the cathode being made of iron. The electrode reactions occurring in this cell are as follows.

(*A*) *Cathode reactions*

$$\text{(i)} \quad H^+ + e = H$$
$$\text{(ii)} \quad 2H = H_2$$

The hydrogen ions quoted in (i) are provided by the dissociation of water—

$$H_2O \rightleftharpoons H^+ + OH'$$

(*B*) *Anode reaction*

$$Na - e = Na^+$$

After the decomposition of the amalgam, the solution contains sodium ions and hydroxyl ions in equivalent concentrations; in other words, sodium hydroxide is present.

Electrolysis of Sodium Hydroxide Solution. When an aqueous solution of sodium hydroxide is electrolyzed between platinum electrodes, hydrogen ions and not sodium ions are discharged at the cathode because of the lower discharge potential of the former. Hydroxyl ions are discharged at the anode and interact with one another to form water and liberate oxygen. These electrode reactions may be depicted as follows—

(*A*) *Cathode reactions*

$$\text{(i)} \quad H^+ + e = H$$
$$\text{(ii)} \quad 2H = H_2$$

(*B*) *Anode reactions*

$$\text{(i)}\ OH' - e = OH$$

$$\text{(ii)}\quad 4OH = 2H_2O + O_2$$

Thus the concentration of sodium hydroxide is progressively increased because of the removal of water as hydrogen and oxygen.

Electrolysis of Copper Sulphate Solution. An aqueous solution of copper sulphate contains cupric ions, sulphate ions, hydrogen ions and hydroxyl ions. On electrolysis of such a solution between platinum electrodes, cupric ions are discharged at the cathode and this electrode becomes coated with metallic copper (it is in fact copper-plated). At the anode, because of the lower discharge potential, hydroxyl ions are discharged in preference to sulphate ions. The hydroxyl ions react with one another to form water and liberate oxygen. The progressive removal of hydroxyl ions in this manner causes more water molecules to dissociate, so increasing the concentration of hydrogen ions. The net result of this electrolysis, bearing in mind the progressive removal of cupric ions, is that the solution of copper sulphate is slowly transformed into a solution of sulphuric acid. The electrode reactions are as follows—

(*A*) *Cathode reaction*

$$Cu^{++} + 2e = Cu$$

(*B*) *Anode reactions*

$$\text{(i)}\ OH' - e = OH$$

$$\text{(ii)}\quad 4OH = 2H_2O + O_2$$

If the anode is made of copper, copper atoms yield electrons and pass into solution as cupric ions—

$$Cu - 2e = Cu^{++}$$

Neither hydroxyl ions nor sulphate ions are discharged at a copper anode since a higher e.m.f. is required in both these cases to effect their discharge than is needed to remove two electrons from each of the copper atoms making up the anode. The progressive dissolution of a copper anode, and the deposition of metallic copper on a cathode in a copper-containing electrolyte, constitute the basis of the technical processes of electrolytic refining of copper and the electrodeposition (or electroplating) of copper.

Faraday's Laws of Electrolysis

The relationship between the quantity of electricity passing through an electrolyte and the quantities of substances liberated at the electrodes was discovered by Faraday whose results are usually stated as follows—

(1) The amount of chemical decomposition produced by an electric current, that is the amount of any substance deposited or dissolved,

is proportional to the quantity of electricity passing through the electrolyte.

(2) The amounts of different substances deposited or liberated by the same quantity of electricity are proportional to their chemical equivalent weights.

When a current of 1 ampere flows for 1 second the quantity of electricity which has passed is termed 1 *coulomb*. The coulomb is the unit of quantity of electricity.

Faraday's First Law may be confirmed by passing through any given solution different currents for various periods of time and determining the weights of material dissolved from the anode or deposited at the cathode; these weights will be found to be proportional to the quantity of electricity used. It is an experimental fact that when 1 coulomb of electricity is passed through solutions of copper sulphate, silver nitrate, and dilute sulphuric acid, the quantities of copper, silver, and hydrogen liberated at the three cathodes are respectively—

Copper	0·32935	milligrammes
Silver	1·118	,,
Hydrogen	0·010446	,,

These quantities are termed the *electrochemical equivalents* of these elements.

Faraday's Second Law states that these weights, the electrochemical equivalents, are proportional to the chemical equivalent weights of the elements concerned. This statement may be tested by dividing the chemical equivalent weights by the corresponding electrochemical equivalents—

Copper	31·79/0·00032935	= 96 494	coulombs
Silver	107·88/0·001118	= 96 494	,,
Hydrogen	1·008/0·000010446	= 96 494	,,

Thus, the very important fact is derived that one gramme equivalent weight of any one of these three elements is liberated by the same quantity of electricity, namely 96 494 coulombs. In view of slight uncertainties such as the presence of small amounts of impurities, the accuracy of the units employed and the accuracy of the atomic weights of the elements in question, it is usual to round off the last two figures and to state that the passage of 96 500 coulombs of electricity will result in the deposition of the gramme equivalent weight of copper, silver, or hydrogen or any other element. This quantity of electricity is termed the *faraday* and is usually denoted by the symbol *F*.

For engineering applications it is often useful to remember that the faraday, as well as being equal to 96 500 coulombs, is also equal to

26·8 ampere-hours. If a current of I amperes flows for t seconds, the number of coulombs passing is It coulombs, so that, by the application of Faraday's Laws of Electrolysis, the weight of material liberated at the cathode will be $It/96\,500$ gramme equivalent weights. If the equivalent weight of the substance in question is E, then the weight of the substance liberated will be $ItE/96\,500$ g.

The Measurement of Quantity of Electricity. The quantity of electricity employed in an electrochemical process may be determined by using an ammeter and noting the time for which the current flows, but this procedure tends to be inaccurate and is often inconvenient. The exact measurement in the laboratory of the quantity of electricity used in an electrochemical process may be made by the use of a *coulometer*.

There are various types of coulometer but the most accurate is probably the silver coulometer. This instrument simply consists of a small platinum basin in which a solution of silver nitrate is electrolyzed under carefully controlled conditions. The platinum basin serves as the cathode whilst a small piece of pure silver foil acts as the anode. From the weight of the silver deposited on the platinum basin the numerical value of the product It may be evaluated by means of the expression—

$$\frac{ItE}{96\,500} = \text{weight of silver deposited (in grammes)} \quad . \quad (1)$$

where It = the quantity of electricity flowing through circuit, and E = equivalent weight of silver (i.e. 107·88).

For many laboratory applications the copper coulometer is used instead of the silver coulometer. The copper coulometer contains an acidified solution of copper sulphate with a small quantity of either ethyl alcohol or tartaric acid to prevent oxidation of the deposited copper. The numerical value of the product It is evaluated in the same manner as described above for the silver coulometer, except that the equivalent weight of copper is employed instead of the equivalent weight of silver.

The faraday is the quantity of electricity carried by one gramme equivalent weight of any univalent ion; but if the valency of the ion is z, then the corresponding gramme ion must contain z gramme equivalents and must, therefore, carry a charge of zF coulombs, where F = one faraday. Thus, the quantity of electricity carried by an ion is the same for all ions of the same valency and is proportional to the valency. Now a univalent positive ion of an element is an atom or a radical which has lost one electron, and a univalent negative ion is an atom or a radical which has gained an electron. Similarly, a bivalent positive ion is an atom or a radical which has lost two electrons, and so on. The number of atoms in the gramme atomic weight of all elements is the same so that the number of electrons associated in electrolysis with the gramme equivalent weight of any element, irrespective of its valency, is the same. Therefore if e is the

charge on the electron and F the quantity of electricity carried by N atoms in the gramme ion, where N is the Avogadro Number, then—

$$Ne = F \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$= 96\,500 \text{ coulombs}$$

This expression may be employed to determine the numerical value of the Avogadro Number—

$$Ne = 96\,500 \text{ coulombs}$$
$$= 9650 \text{ electromagnetic units}$$
$$= 9650 \times 2{\cdot}998 \times 10^{10} \text{ electrostatic units}$$

where $2{\cdot}998 \times 10^{10}$ = velocity of light in centimetres per second.

$$N = \frac{9650 \times 2{\cdot}998 \times 10^{10}}{4{\cdot}774 \times 10^{-10}}$$

where e = charge on electron = $4{\cdot}774 \times 10^{-10}$ electrostatic units.

Therefore $$N = 6{\cdot}059 \times 10^{23}$$

The Mechanism of Electrolytic Conduction

Van't Hoff (1885) pointed out that theoretically and practically the Gas Laws are approximately applicable to dilute solutions of organic solutes, although this generalization does not hold for electrolytes. Thus, if one gramme molecule of solute is dissolved in V litres of solvent, then the osmotic pressure P of the solution at absolute temperature T is given by the expression—

$$PV = RT \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where R = the gas constant.

In the case of electrolytes, the value of the osmotic pressure calculated by means of equation (3) is always greater than P, sometimes being greater than $2P$, although a value of $3P$ has never been attained experimentally. It will be recalled (*see* p. 158) that similar anomalies are also found in the lowering of vapour pressure, depression of the freezing point, and elevation of the boiling point, since all these properties are fundamentally connected with osmotic pressure. To overcome this difficulty van't Hoff introduced the empirical factor i into the Gas Law equation (3). This factor, often known as the van't Hoff factor or coefficient, varies with the concentration of the solution. The amended Gas Law equation therefore becomes—

$$PV = iRT \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Noting the significance of van't Hoff's results, Arrhenius (1887) proposed his Theory of Electrolytic Dissociation in which he suggested that when

an electrolyte is dissolved in water, a considerable portion of the solute is spontaneously dissociated into positive and negative ions; that is—

$$AB \rightleftharpoons A^+ + B'$$

and these ions, each being capable of independent movement, migrate under the influence of an applied potential to electrodes of opposite electrical sign. The proportion of the molecules which dissociated into ions was considered to vary with the concentration of the solution, the fraction of the total electrolyte split up into ions, that is, the *degree of dissociation*, being thought to approach unity at infinite dilution. In other words, at extreme dilution the whole of the electrolyte was considered to be completely dissociated into ions.

Suppose each molecule of an electrolyte when it dissociates yields v ions. Then, if a solution contains a total of m molecules in a given volume, and α is the fraction dissociated (i.e. the degree of dissociation), there will be present $vm\alpha$ ions and $m(1-\alpha)$ undissociated molecules. Thus, the total number of particles present is $m(1-\alpha+v\alpha)$. Now, the van't Hoff factor, i, is given by the ratio of the observed to the calculated osmotic pressure, thus—

$$i = \frac{\text{Observed osmotic pressure}}{\text{Calculated osmotic pressure}} \left(= \frac{\text{Observed boiling-point elevation}}{\text{Calculated boiling-point elevation}} = \frac{\text{Observed freezing-point depression}}{\text{Calculated freezing-point depression}} = \frac{\text{Observed effect}}{\text{Calculated effect}} \right)$$

Therefore, the osmotic pressure of a solution (like gas pressure) is proportional to the number of individual particles in a given volume; that is—

$$i = \frac{\text{Number of particles present}}{\text{Number of particles which would have been present if dissociation had not occurred}}$$

$$= \frac{m(1-\alpha+v\alpha)}{m}$$

$$= 1-\alpha+v\alpha$$

and $$\alpha = \frac{i-1}{v-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The value of the van't Hoff factor i may be evaluated from measurements of osmotic pressure, depression of the freezing point or elevation of the boiling point, whilst the numerical value of v is obtained by inspection of the formula of the solute.

By means of equation (5) Arrhenius calculated, for various electrolytes at a number of concentrations, the numerical value of α which he considered

to be the degree of dissociation. He also calculated the numerical value of α from measurements of the electrical conductance of the same solutions. Although Arrhenius regarded the concordance between the two series of results as satisfactory evidence for his Theory of Electrolytic Dissociation, it is now considered that this agreement is largely coincidental.

The Conductance of Electrolytes. Electrolytes, like electronic conductors obey Ohm's Law, except under such abnormal conditions as those involving very high voltages and/or very high frequency alternating currents. The conductance of an electrolyte is calculated from measurements of its resistance.

A current flowing through a conductor under the influence of a constant e.m.f. is inversely proportional to the resistance of that conductor. If the resistance of the conductor is denoted by R, then the quantity $1/R$ is a measure of its conducting power, this quantity is called the *conductance.* Whilst resistances are usually expressed in ohms, conductances are quoted in *reciprocal ohms* or *mhos.*

The resistance R of any conductor varies directly as its length, and inversely as its area—

$$R = \frac{\rho l}{a} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where l = length of conductor in centimetres, a = cross-sectional area of conductor in square centimetres, ρ = a constant for any given conductor known as *specific resistance* or *resistivity.* The specific resistance of any given conductor is the resistance in ohms of a specimen of the material, 1 cm long and 1 cm^2 in cross section. In other words, the specific resistance ρ of a conductor is the resistance of a centimetre cube.

If the conductance $C = \frac{1}{R}$

then the specific conductance,

$$\kappa = \frac{1}{\rho} \text{ (in reciprocal ohms)} \quad . \quad . \quad . \quad (7)$$

Therefore, (6) may be rewritten—

$$R = \frac{l}{\kappa a} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and, the conductance,

$$C = \frac{1}{R} = \frac{\kappa a}{l} \text{ (reciprocal ohms)} \quad . \quad . \quad . \quad (9)$$

The conductance of an electrolyte varies with its concentration, and with the object of making allowance for this effect it is usual to make comparisons of the "equivalent conductance." The equivalent conductance, Λ_v

at the dilution v is a measure of the conducting power of all the ions resulting from the dissociation of 1 gramme equivalent weight of the solute when present in a volume of v millilitres of solution.

Since
$$C = \frac{\kappa a}{l} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

then, if l is 1 cm, the volume of v ml of solution will occupy an area of v cm^2 of the two electrodes, so that—

$$\Lambda_v = \kappa v \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and if c is the concentration of the solute in gramme equivalents per litre, then—

$$\Lambda_v = \frac{1000\kappa}{c} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Expressed in words, the equivalent conductance is numerically equal to the product of the specific conductance and the volume in millilitres containing one gramme equivalent weight of the solute. In a similar manner, the "molecular conductance" (or molar conductance), μ, may be shown to be equal to the product of the specific conductance and the volume in millilitres containing one gramme molecular weight of solute.

It should be noted that for uni-univalent electrolytes the values of Λ and μ are identical since the gramme equivalent weight and the gramme molecular weight are the same. In the case of uni-bivalent and bi-univalent electrolytes the equivalent conductance is half the molecular conductance since the equivalent weight of such compounds is half the molecular weight.

The Experimental Determination of Electrolytic Conductance. The conductance of an electrolyte is generally determined experimentally by means of a circuit involving a Wheatstone bridge. If a direct current supply is used for the bridge the electrodes of the cell containing the electrolyte under examination are said to become *polarized* in that the products of the electrolysis collect at the electrodes and set up a back e.m.f. which has the effect of increasing the apparent resistance of the electrolyte. With the object of overcoming such sources of error due to polarization it is usual to employ an alternating current supply for the bridge circuit and by means of this technique the polarization set up by each current pulse is neutralized by the next pulse. The alternating current supply may be provided by a small induction coil, although a small valve oscillator is to be preferred.

The general arrangement of the apparatus is shown diagrammatically in Fig. 95, in which A is the cell containing the electrolyte under investigation, B is a resistance box, XZ is a uniform graduated resistance wire, and

D is the current detector which may either be an a.c. galvanometer, or a telephone receiver, or alternatively the output from the points *a* and *b* (Fig. 95) may be connected through a triode valve to a "Magic Eye" tuning indicator (a miniature cathode-ray oscilloscope). This latter method of current detection is probably the most sensitive.

The source of alternating current is connected to the bridge network at the points *X* and *Z* and the resistance of *B* varied in conjunction with adjustment of the contact *Y* on the slide wire *XZ* until the position of minimum current is obtained as indicated by *D*; this will be minimum deflection in an a.c. galvanometer, or minimum sound in a telephone receiver, or minimum area of fluorescence in a "Magic Eye" tuning indicator. When examining electrolytes of low conductance a sharp point of balance is difficult to obtain unless the electrostatic capacity of the cell *A* is compensated for in the opposite arm of the bridge by means of a small variable condenser *C*. The resistance *B* should be of such magnitude that the bridge is balanced when the contact *Y* occupies a position as close as possible to the mid-point of *XZ*. When these conditions obtain, then—

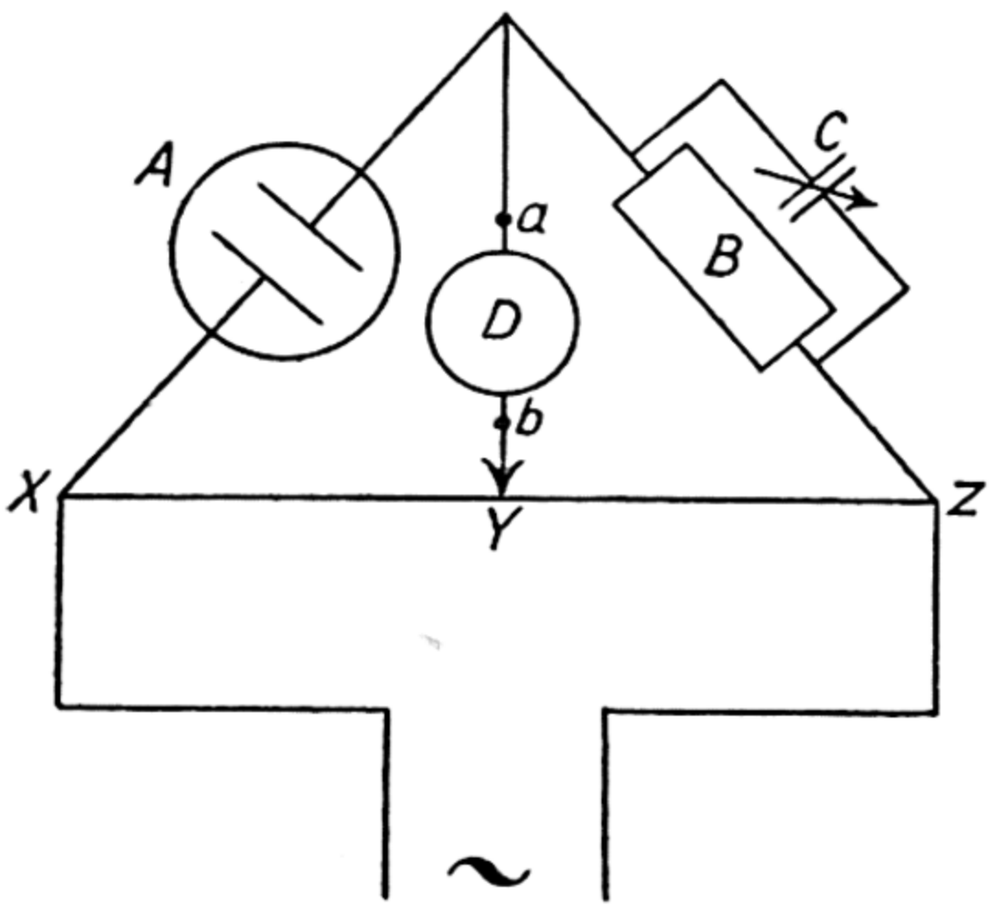


FIG. 95. Circuit for Determination of Electrolytic Conductance

$$\frac{\text{The resistance of } A}{\text{The resistance of B}} = \frac{\text{The length } XY}{\text{The length } YZ}$$

Therefore,

$$\text{The resistance of } A = \frac{\text{The length } XY \times \text{The resistance of } B}{\text{The length } YZ}$$

Conductance Cells. Although various types of conductance cells have been employed for conductance measurements, the simple type of cell as shown in Fig. 96 is satisfactory for most purposes. The cell itself is made either of chemical resistance glass or of fused silica. The electrodes are of platinum foil, fixed rigidly with respect to one another; with the object of minimizing the effect of polarization the electrodes are often coated with platinum black. This is usually deposited by electrolysis of a 3 per cent aqueous solution of chloroplatinic acid, each of the electrodes being made alternately anode and cathode. When examining certain electrolytes, platinized electrodes cannot be used since platinum black may catalyze the decomposition or oxidation of the electrolyte.

Conductance Water. In making up solutions for submission to conductance measurements it is necessary to use specially pure water known as *conductance water*. The purest water, known as "ultra-pure water" has a specific conductance of $0{\cdot}05 \times 10^{-6}$ mhos at 18°C but this water is exceedingly difficult to maintain pure and is only necessary for the most precise work. For most determinations, however, a sufficiently pure water can be prepared by re-distilling good distilled water, to which has been

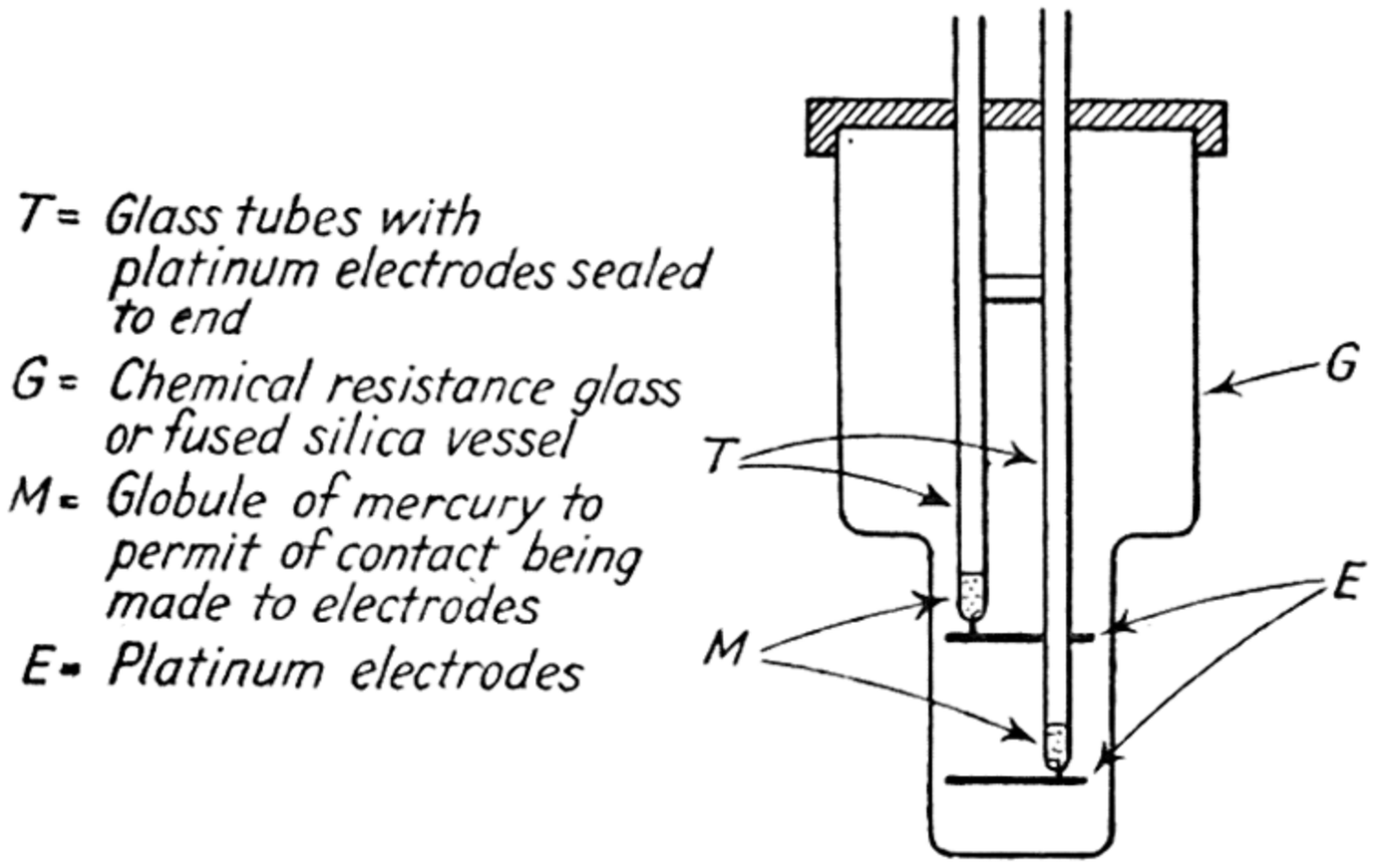


FIG. 96. Conductance Cell

added a little potassium permanganate, in a still constructed of chemical resistance glass. Alternatively it may be prepared by the use of de-ionizing resins (*see* p. 512). Such water, which has a specific conductance of $0{\cdot}8 \times 10^{-6}$ mhos at 18°C, due chiefly to dissolved carbon dioxide, is known as *equilibrium water*.

The Cell Constant.

Since
$$R = \frac{l}{\kappa a} \quad . \quad . \quad . \quad . \quad . \quad (8)$$
$$\kappa = \frac{l}{aR} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where l = the distance apart of two similar electrodes and a = the area of cross-section of each electrode.

The quantity, l/a is called the *cell constant*. The cell constant may be determined by direct measurement of l and a, but this is rarely done since it is possible to evaluate this quantity by measuring the resistance of a solution of known specific conductance (e.g. potassium chloride). If a given aqueous solution of potassium chloride of specific conductance κ_0 is placed in the conductance cell and its resistance by measurement is found to be R_0, then by equation (12) above, it follows that the cell constant K is equal to $\kappa_0 R_0$. If the resistance of any other electrolyte is found by measurement to be R_x when using the same conductance cell, then the

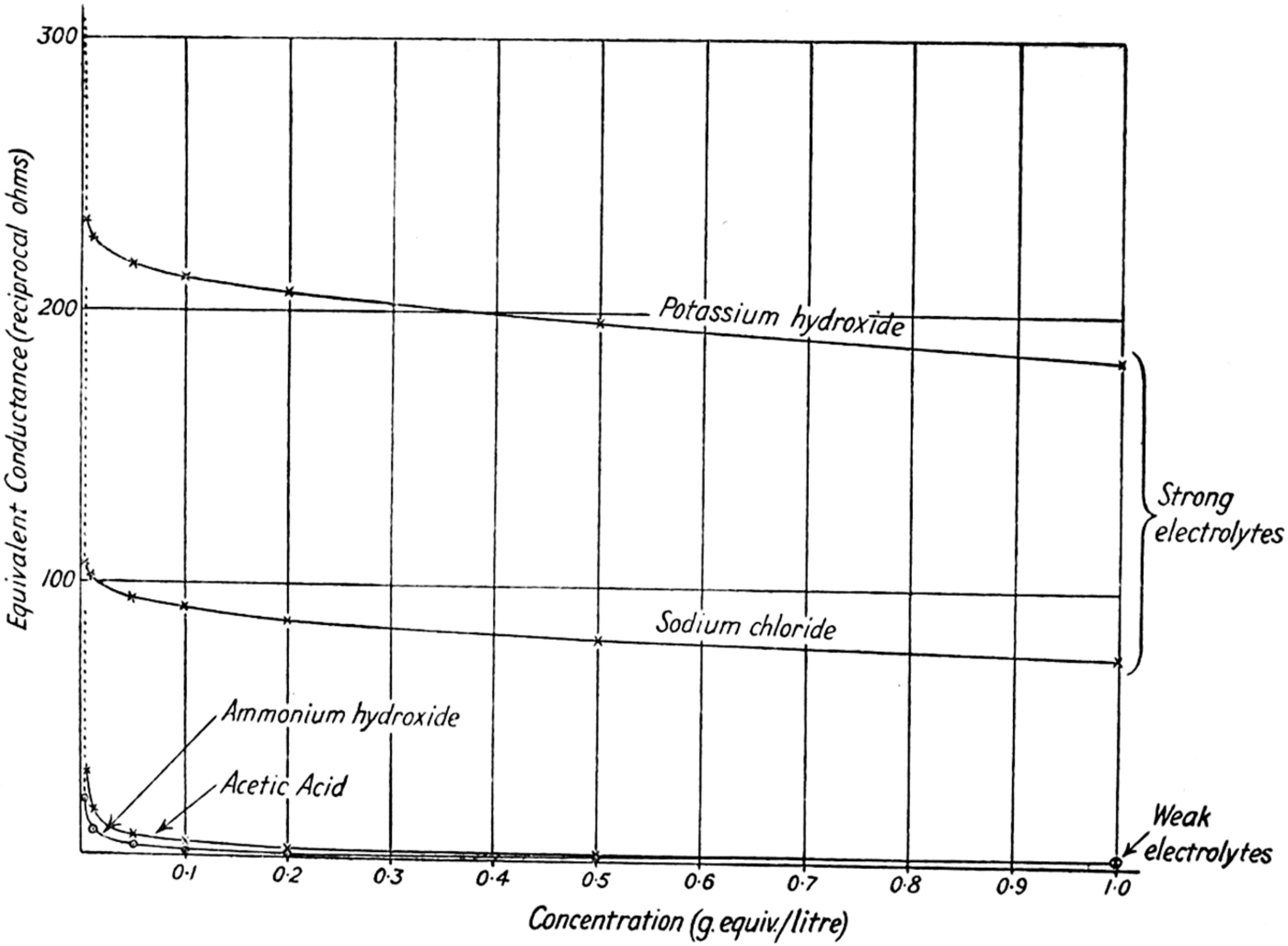


FIG. 97. Variation with Concentration of Equivalent Conductance at 18°C

specific conductance of this electrolyte is K/R_x. Thus, on multiplying the value of the specific conductance so obtained by v, the volume of solution in millilitres containing one gramme equivalent weight of the electrolyte under investigation, the equivalent conductance Λ_v is evaluated.

The Results of Conductance Measurements. It is found experimentally that although with decreasing concentration the conductance of an electrolyte becomes progressively smaller, the values of the equivalent conductance and the molecular conductance increase as the concentration decreases until a maximum limiting value is finally attained. Some typical values are given in Table 47.

TABLE 47

Typical Values of Equivalent Conductance (after Glasstone)
(in reciprocal ohms)

Concentration of Electrolyte (g equiv/litre)	HCl	KOH	NaCl	$\frac{1}{2}K_2SO_4$	$\frac{1}{2}CuSO_4$	$CH_3.COOH$	NH_4OH
0·001	377·0	234	106·3	126·7	98·4	41·0	28·0
0·002	375·5	233	105·3	124·4	91·8	30·2	20·6
0·01	369·3	228	101·7	115·6	71·6	14·3	9·6
0·05	357·6	218	95·5	101·8	51·1	6·48	4·6
0·1	350·1	213	91·8	94·8	43·8	4·60	3·3
0·2	341·5	207	87·5	87·8	37·6	3·24	2·30
0·5	326·6	197	80·8	78·3	30·7	2·01	1·35
1·0	300·5	184	74·2	71·5	25·7	1·32	0·89

The results for four electrolytes have been plotted in Fig. 97 and it will be noted that in the case of potassium hydroxide and sodium chloride the variation of equivalent conductance with concentration is not very large; this phenomenon is exhibited by all strong acids, strong bases, and most salts. Such substances are known as *strong electrolytes*. On the other hand, in the case of ammonium hydroxide and acetic acid the equivalent conductance falls off rapidly with increasing concentration until at a concentration of one gramme equivalent per litre the value of the equivalent conductance is very low indeed. All weak acids and weak bases resemble ammonium hydroxide and acetic acid in these respects. Such substances are termed *weak electrolytes*. It is to be noted, however, that there is no sharp line of demarcation between these two types of electrolytes.

The limiting value of the equivalent conductance which is attained with decreasing concentration is termed the equivalent conductance at *infinite dilution*, and is denoted by the symbol Λ_0.* The determination of Λ_0

* When the strength of a solution is expressed in terms of a concentration the symbols Λ_c and Λ_o are employed; when the strength of a solution is expressed in terms of a dilution the symbols Λ_v and Λ_∞ are used instead.

involves the extrapolation to zero concentration of values for the equivalent conductance of dilute solutions. This may be done by plotting values for the equivalent conductance against the square root of the concentration since this plot gives a straight line at low concentrations. In the case of weak electrolytes this extrapolation technique does not permit of the evaluation of Λ_0 with sufficient precision and use has to be made of ion conductances as described on p. 256.

The Conductance Ratio. The conductance of an electrolyte depends not only upon the actual number of ions present, but also upon the velocity of these ions, that is the ease with which they pass through the solution. Arrhenius assumed that the velocities of ions are constant so that the only reason for increase in equivalent conductance with decreasing concentration must be the production of more ions, until at infinite dilution he suggested that the electrolyte was completely dissociated. From these assumptions Arrhenius suggested that the degree of dissociation was given by—

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_c}{\Lambda_0} \text{ or expressed as a dilution} = \frac{\Lambda_v}{\Lambda_\infty}$$

Research has shown however that the ionic velocities are *not* constant because of the mutual attraction of ions at appreciable concentration; and the ratio Λ_c/Λ_0 is no longer regarded as indicating the degree of dissociation. Instead this ratio is known by the name *conductance ratio*. In fact, as far as strong electrolytes are concerned, the conductance ratio is probably a better index of the change in the speeds of the ions rather than of their number.

In the case of weak electrolytes, however, the number of ions is relatively small and so also is the interionic attraction leading to a reduction of ionic speeds. For such electrolytes, therefore, the ionic velocities are not much affected by variation in concentration with the result that, provided the solution is neither too dilute nor too concentrated, the conductance ratio is a reasonably good index of the degree of dissociation.

The Independent Migration of Ions. If equivalent conductances at infinite dilution of some pairs of salts having one ion in common are examined, certain regularities are to be observed. Some examples are quoted in Table 48.

From Table 48 it will be noted that the differences between the values of Λ_0 for the sodium and potassium salts of the same anion are constant and independent of the nature of the anion. Likewise, the differences between the values of Λ_0 for chlorides and sulphates of a given cation are similarly independent of the nature of the cation.

These phenomena, discovered by Kohlrausch (1876) led him to suggest that *every ion at infinite dilution contributes a definite amount towards the equivalent conductance, irrespective of the nature of the other ion with which*

TABLE 48

Equivalent Conductances at Infinite Dilution at 18°*C*
(*in reciprocal ohms*)

Electrolyte	Λ_0	Electrolyte	Λ_0	Difference
KCl	130·0	NaCl	108·9	21·1
KNO_3	126·3	$NaNO_3$	105·2	21·1
$\frac{1}{2}K_2SO_4$	133·0	$\frac{1}{2}Na_2SO_4$	111·9	21·1
KCl	130·0	$\frac{1}{2}K_2SO_4$	133·0	3·0
NaCl	108·9	$\frac{1}{2}Na_2SO_4$	111·9	3·0

it is associated in the electrolyte. This statement, which is known as Kohlrausch's *Law of Independent Migration of Ions*, may be expressed mathematically as follows—

$$\Lambda_0 = l_+ + l_- \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where l_+ and l_- are the so-called *ion conductances*, at infinite dilution, of the cation and anion respectively. These ion conductances are the amounts contributed by each ion, independently of the other, to the total equivalent conductance.

The conductance of an electrolyte depends upon three factors—

(*a*) The number of ions;
(*b*) The charge carried by each ion;
(*c*) The velocity at which the ions move.

Since in each case the total charge is a constant the equivalent conductance of an electrolyte at infinite dilution must depend solely upon the speeds of its ions, and it is the difference in the speeds of the ions which is responsible for the different values of Λ_0 as given in Table 48. Thus, if u and v are the velocities of cation and anion respectively under a fall of potential of 1 volt/cm the values of Λ_0 must be proportional to the sum of these two velocities. Expressed mathematically—

$$\Lambda_0 = k(u + v)$$
$$= ku + kv \quad . \quad . \quad . \quad . \quad (14)$$

where k is a constant which is the same for all electrolytes, the cation contribution to conductance being ku, whilst the anion contribution to conductance is kv.

It follows, therefore, from the identity of equations (13) and (14) that,

$$l_+ = ku$$

and

$$l_- = kv$$

In other words, the ion conductance is proportional to the velocity of the ion.

Ion conductances are often referred to as *ionic mobilities* on account of the relationship of ion conductances to the velocities at which the ions migrate under the influence of an applied e.m.f. Ion conductances are also related to transport numbers (*see* p. 259) as follows—

$$t_+ = \frac{l_+}{\Lambda_0} \text{ and } t_- = \frac{l_-}{\Lambda_0} \quad . \quad . \quad . \quad . \quad (15)$$

where t_+ and t_- are the transport numbers for the cation and anion respectively. From a consideration of data for strong electrolytes it is possible by utilizing (15) to calculate values for ion conductances for a large number of ions. Some typical values are given in Table 49.

TABLE 49

Ion Conductances at Infinite Dilution at 18°C

Cation	l_+ (r.ohms)	Anion	l_- (r.ohms)
H^+	315·2	OH'	173·8
Cs^+	67·46	I'	66·25
K^+	64·20	Br'	67·31
NH_4^+	64·3	Cl'	65·24
Na^+	43·16	F'	46·6
Li^+	33·02	NO_3'	61·62
Ag^+	53·8	CH_3COO'	35·0
$\frac{1}{2}Ba^{++}$	55·0	$\frac{1}{2}SO_4''$	68·5
$\frac{1}{2}Pb^{++}$	61·0	$\frac{1}{2}CO_3''$	60·0

Since the value of Λ_0 increases with rising temperature the value of ion conductance also increases as the temperature rises, and at elevated temperatures all ions tend to have the same conductance. As was stated previously (*see* p. 254) the numerical value of Λ_0 for a weak electrolyte cannot be obtained directly from measurements of its conductance. It is, however, possible to effect its computation from known values of ion conductances. For example (introducing values from Table 49), the value of Λ_0 for acetic acid may be calculated as follows—

$$\begin{aligned} \Lambda_{0\,(CH_3.COOH)} &= l_{H^+} + l_{CH_3.COO'} \\ &= 315{\cdot}2 + 35{\cdot}0 \\ &= 350{\cdot}2 \text{ r.ohms at } 18°C \end{aligned}$$

Alternatively, by application of Kohlrausch's Law of Independent Migration of Ions—

$$\begin{aligned}\Lambda_{0\,(CH_3.COOH)} &= \Lambda_{0\,(HCl)} + \Lambda_{0\,(CH_3.COONa)} - \Lambda_{0\,(NaCl)} \quad . \quad (16)\\ &= (l_{H^+} + l_{Cl'}) + (l_{Na^+} + l_{CH_3.COO'}) - (l_{Na^+} + l_{Cl'})\\ &= l_{H^+} + l_{CH_3.COO'}\end{aligned}$$

Thus, by introducing values of Λ_0 for the three strong electrolytes, hydrochloric acid, sodium acetate and sodium chloride in (16), the value for Λ_0 for acetic acid may be evaluated.

The Solvation of Ions. Since the equivalent conductance of an ion at infinite dilution depends only upon its speed, *the product of ion conductance and viscosity should be independent of the character of the solvent.* This relationship, known as *Walden's Rule*, is however only approximately true as is shown by Table 50.

Expressed mathematically, Walden's Rule is—

$$\Lambda_0\eta_0 = \text{a constant for any given electrolyte}$$

where η_0 is the viscosity of the solvent in which the equivalent conductance at infinite dilution is Λ_0.

TABLE 50

Product of Ion Conductance and Viscosity at 25°C

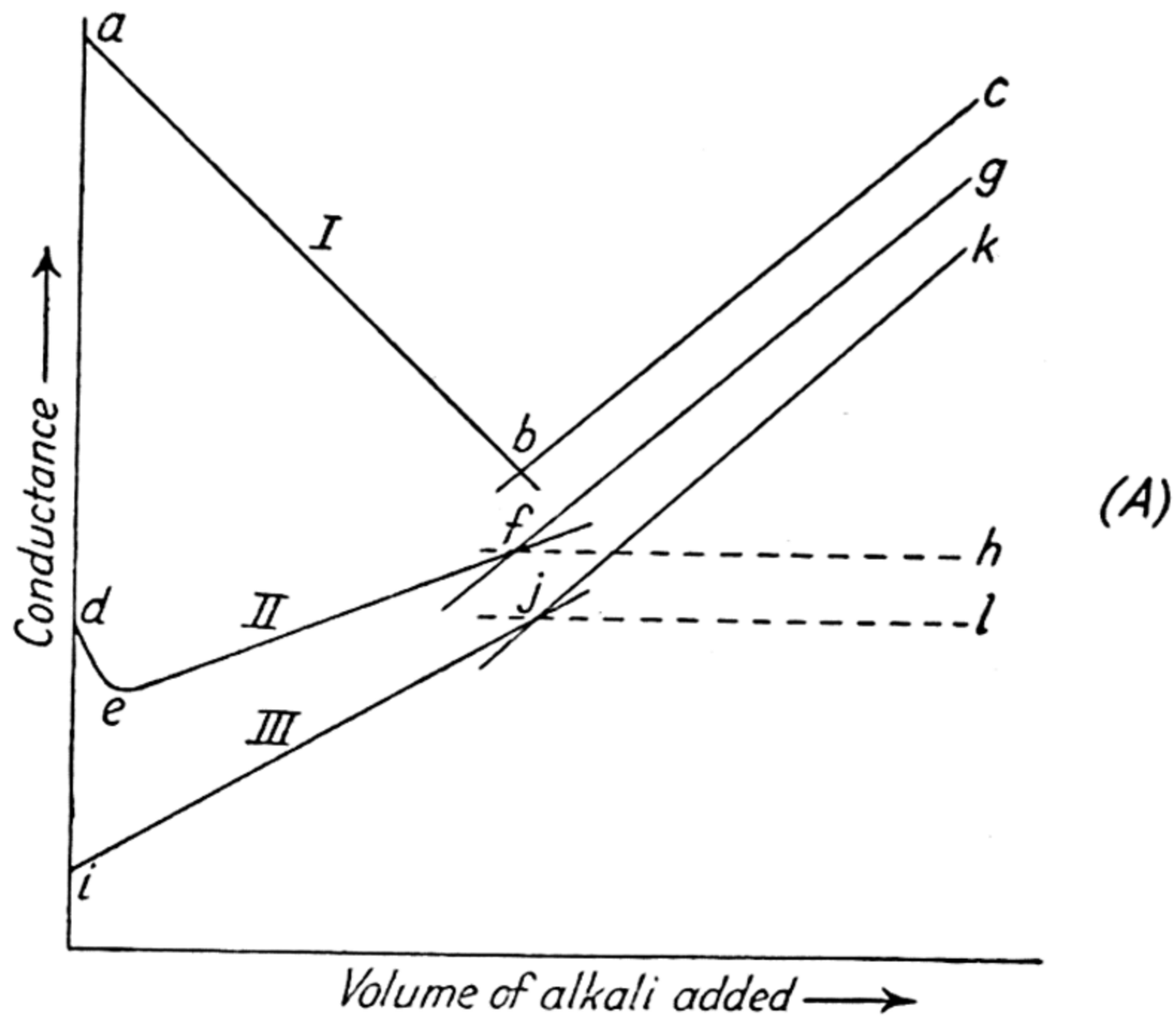
Solvent	H^+	Li^+	Na^+	NH_4^+	Cl'	NO_3'
Water . . .	3·14	0·36	0·46	0·66	0·69	0·63
Methyl alcohol .	0·78	0·22	0·26	0·32	0·29	0·83
Ethyl alcohol . .	0·67	0·16	0·20	0·20	0·26	0·28
Acetone . .	0·28	0·22	0·22	0·28	0·33	

The lack of constancy in the case of each ion in different solvents clearly shows the limitations of Walden's Rule, and indicates that an ion does not necessarily have the same effective radius in different solvents. These variations are due to differing degrees of solvation which each ion suffers in different solvents. In other words, since an ion is capable of attaching to itself one or more molecules of solvent, according to the nature of the solvent, the effective radius of the solvated ion will not be constant; this will affect its mobility, so that the product $\Lambda_0\eta_0$ cannot be expected to be constant.

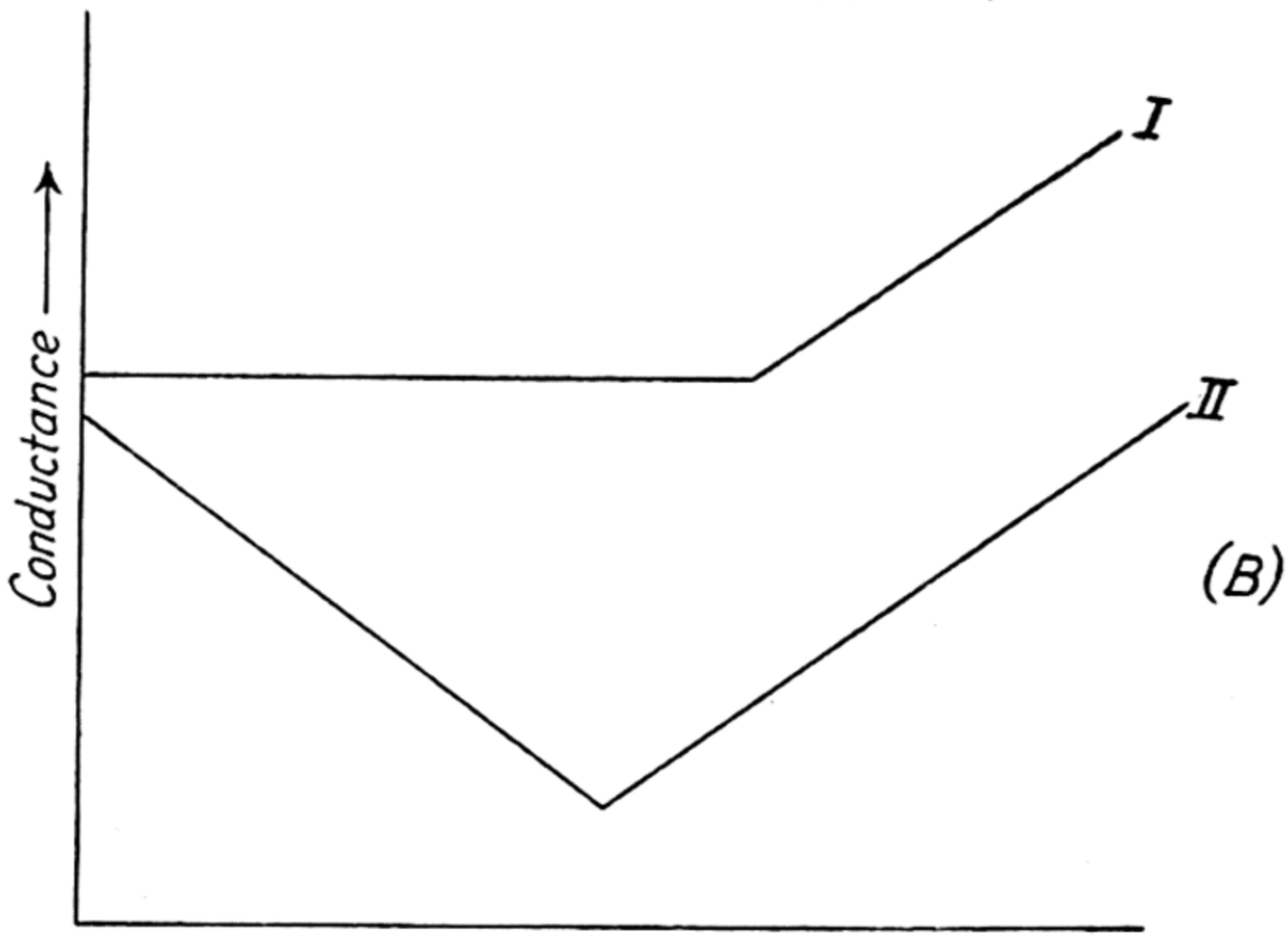
Conductometric Analysis

A knowledge of ion conductances may be applied to the chemical analysis of solutions by means of the technique known as *conductometric analysis.* Thus, the addition of an alkali to a strong acid causes the replacement of the highly conducting hydrogen ions of the acid by metal ions of a much

lower conductance; the conductance of the solution therefore progressively falls (*see* portion *ab* of curve I—Fig. 98 (*A*)). When neutralization of the acid is completed, the addition of more alkali causes the conductance to



(A)



(B)

FIG. 98. Conductometric Analysis Curves

increase again—portion *bc*—since there are now present the highly conducting hydroxyl ions; thus the endpoint of the neutralization is marked by a minimum in the conductance.

When a weak acid (e.g. acetic acid) is neutralized, the conductance shows an initial fall (*see* portion *de* of curve II in Fig. 98 (*A*)), since the formation of the salt having an ion in common with the acid tends to

repress the dissociation of the acid. After this initial fall the conductance increases—portion *ef*—since the highly dissociated salt being produced exhibits a greater conductance than the weak acid undergoing neutralization. If a strong alkali is being employed to neutralize the weak acid the conductance increases more rapidly as soon as the endpoint has been passed—portion *fg*; on the other hand, if a weak alkali is being employed the conductance is almost constant after passing the endpoint—portion *fh*—since such a base exhibits little conductance. If the acid is very weak the initial conductance of the solution is very small and the conductance shows a progressive rise to the endpoint (*see* portion *ij* of Curve III in Fig. 98 (*A*)). After the endpoint, the conductance rises rapidly if a strong base is being employed for the neutralization—portion *jk*; or alternatively, it remains more or less constant if a weak base is being employed—portion *jl*.

From Fig. 98 (*A*) it will be clear that when titrating weak acids it is an advantage to employ a weak base since thereby it is only necessary to take about six or eight readings through which straight lines may then be drawn.

Conductometric analysis finds considerable application when dealing with coloured solutions in which changes in indicator colours could not readily be noted. In addition, mixtures of strong and weak acids may readily be analysed. If sodium chloride solution is added to a solution of silver nitrate the conductance remains almost constant until the whole of the silver has been precipitated as chloride when the conductance rises; this is indicated graphically in Fig. 98 (*B*)—curve I.

$$NaCl + AgNO_3 = NaNO_3 + AgCl\downarrow$$

On the other hand, if both the products of the reaction are only slightly soluble, as in the following case—

$$MgSO_4 + Ba(OH)_2 = Mg(OH)_2\downarrow + BaSO_4\downarrow$$

the conductance curve shows a fall until the whole of the magnesium is precipitated as hydroxide after which the conductance rises owing to the presence of free barium hydroxide. The conductance curve for this type of reaction is shown in Fig. 98 (*B*)—curve II.

Transport Numbers (or Transference Numbers). Hittorf (1853) showed that the velocity of ions undergoing migration can be correlated with the changes in concentration in the vicinity of the electrodes. A rapidly moving ion will cause a greater lowering of concentration in the electrode compartment from which it moves than will a slower moving ion. If the speed of the cation is u and that of the anion v, then the total current is proportional to $(u + v)$. The fraction of the total current carried by the cation is $u/(u + v)$, this quantity being known as the *transport number* (or *transference number*) of the cation, and being designated t_+, or t_c. Similarly, the transport number of the anion, t_- or t_a, is equal to $v/(u + v)$. The sum of the two transport numbers is equal to unity.

It is almost invariably found that in any given electrolyte the anions and cations move with different speeds, and yet it is an experimental fact that equivalent quantities of anions and cations are discharged at the anode and cathode respectively in accordance with Faraday's Laws.

The reconciliation of these two apparently conflicting facts may be understood most clearly by means of a diagram (*see* Fig. 99). In this diagram suppose that the electrolyte contained between the anode and

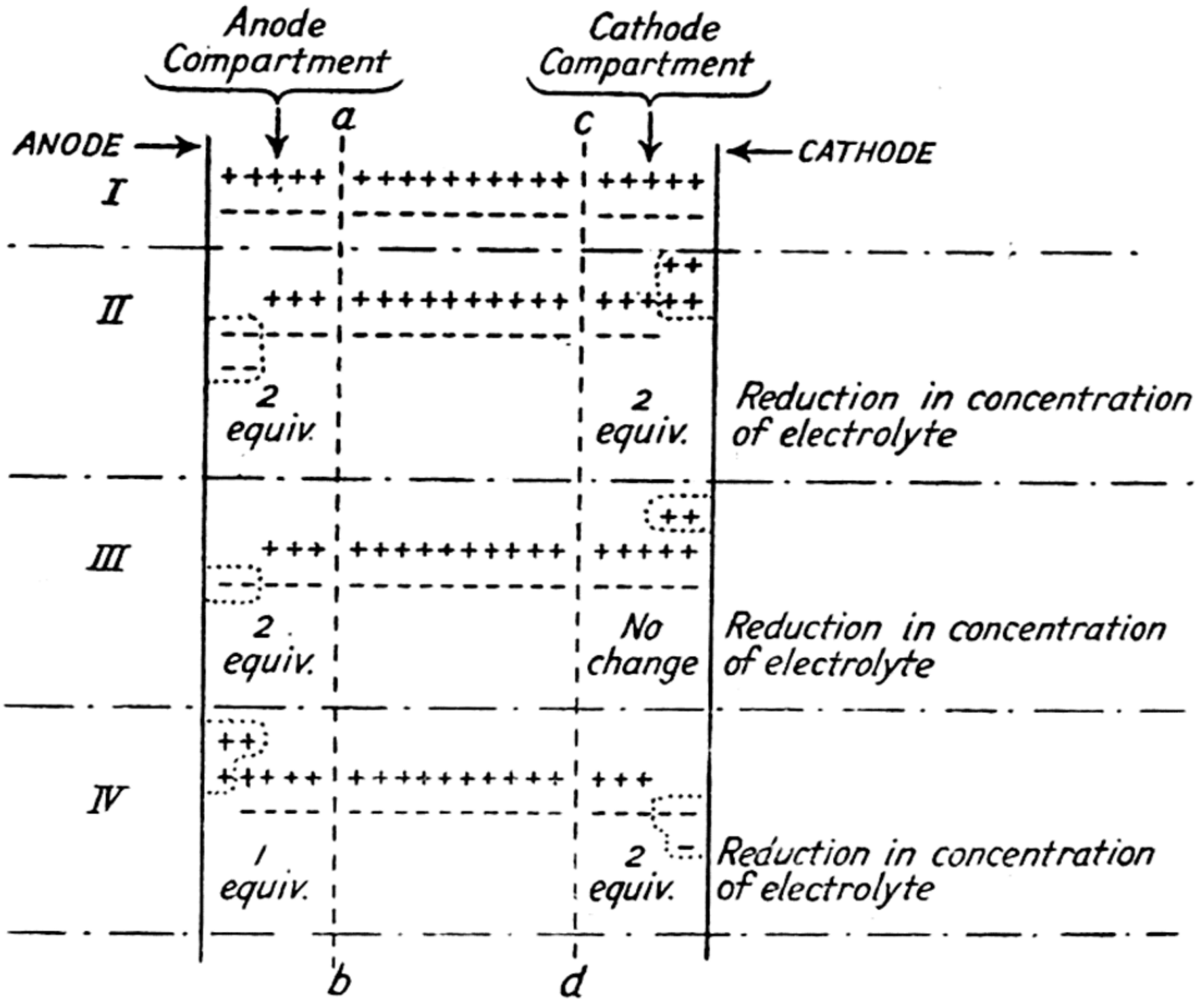


FIG. 99. Diagram illustrating Migration of Ions

cathode is divided by two imaginary partitions *ab* and *cd* into three compartments. Before electrolysis commences the state of the electrolyte is shown at I where each anion is associated with a cation.

Suppose that a potential is now applied to the two electrodes and that in this case the anions and cations all migrate with the same velocity towards the anode and cathode respectively. After a brief interval of time the state as depicted at II may exist in which two anions and two cations have been discharged at the anode and cathode respectively. Suppose, however, that only the cations are able to migrate under the influence of an e.m.f., then the condition attained is that depicted at III, from which it will be noted that if two cations move towards the cathode, two anions will be left unpartnered in the anode compartment, and these must therefore be considered to be discharged in exactly the same way as the two cations. This phenomenon actually occurs in certain fused and solid

electrolytes in which the whole of the current is carried by one type of ion. Suppose, now, that the speed of the anion is twice that of the cation, that is, that two anions are discharged for one cation, the state of the electrolyte will then be that shown at IV.

From a consideration of IV it is noted that it is possible for the same number of ions to be discharged at each electrode, even though the speeds of the anion and cation are different; there is, therefore no conflict between differences of ionic velocity and Faraday's Laws. Examination of Fig. 99, section II, shows that the concentration of the electrolyte in both the anode compartment and also the cathode compartment has decreased by same amount—two equivalents; in section III, however, the concentration of the electrolyte in the anode compartment has diminished by two equivalents, whilst that in the cathode compartment has not suffered any change. In the case of section IV the electrolyte in the anode compartment has decreased in concentration by one equivalent whilst that in the cathode compartment has decreased by two equivalents; expressed mathematically—

$$\frac{\text{Fall in concentration in the anode compartment}}{\text{Fall in concentration in the cathode compartment}} = \frac{1}{2} = \frac{\text{Speed of the cation}}{\text{Speed of the anion}} \quad . \quad (17)$$

$$= \frac{t_+}{t_-} \text{ or, } \frac{t_c}{t_a} \quad . \quad . \quad . \quad (18)$$

Recalling that— $t_c + t_a = 1$

then

$$\frac{\text{Fall in concentration in anode compartment}}{\text{Total fall in concentration in anode and cathode compartments}} = \frac{t_+}{1} = t_+ \quad . \quad (19)$$

$$= \frac{\text{Number of gramme equivalents of electrolyte lost from anode compartment}}{\text{Number of gramme equivalents deposited on each electrode}} \quad . \quad (20)$$

If a coulometer is included in the circuit, then from Faraday's Laws it follows that the same number of gramme equivalents of material, no matter what its nature, will be deposited in the coulometer as in the transport apparatus; therefore—

$$\frac{\text{Number of gramme equivalents of electrolyte lost from anode compartment}}{\text{Number of gramme equivalents of metal deposited in coulometer}} = t_+ \quad . \quad (21)$$

and, in a similar manner it may be deduced that

$$\frac{\text{Number of gramme equivalents of electrolyte lost from cathode compartment}}{\text{Number of gramme equivalents of metal deposited in coulometer}} = t_- \quad . \quad (22)$$

Since the sum of the two transport numbers is equal to unity it is not usually necessary to determine experimentally the transport numbers for both an ion and cation; instead one or the other is determined experimentally and then this value subtracted from unity when the value for the other type of ion is immediately obtained.

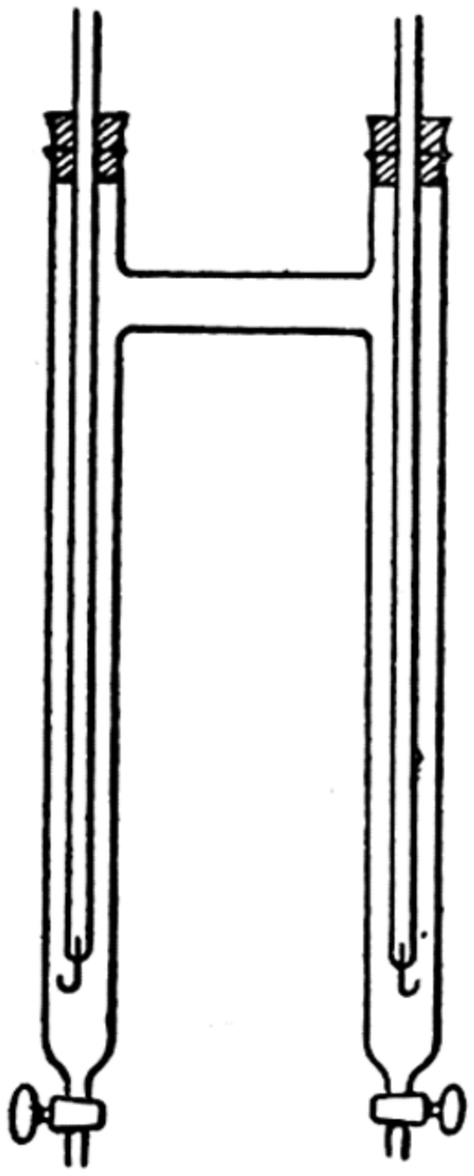


FIG. 100. Apparatus for Determination of Transport Numbers

The Experimental Determination of Transport Numbers. A common form of apparatus employed for the determination of transport numbers is shown in Fig. 100. It consists essentially of two tubes, each about 1·5 cm in diameter and capable of holding 50–100 ml of solution. These two tubes are connected by means of a bridge near the top of each. Both the tubes are fitted with taps at their lower ends to facilitate the withdrawal of the solution. Metal electrodes, fused into the lower ends of narrow bore glass tubes, are inserted into the upper ends of each of the tubes, and maintained in position by means of stoppers. The metal used for the electrodes varies with the electrolyte undergoing examination; for example, for halides of alkali metals, silver is suitable for the anode and silver coated with silver chloride for the cathode, whilst if the electrolyte is silver nitrate, silver may be employed for both anode and cathode. Similarly in the case of other metals capable of being deposited at the cathode and dissolved at the anode, the metal itself may be employed for the electrodes.

The general arrangement of the apparatus used for transport number determinations is shown in Fig. 101. In use, the electrolyte under examination is placed in the limbs of the transport number apparatus which is then immersed in a thermostat. The electrodes are connected in series with either a silver or a copper coulometer (Fig. 101 at *C*) and a small d.c. current of 10–20 milliamperes passed for 3–4 hours. A supply voltage of 50–100 volts from a battery, *B*, is adjusted by the variable resistance *R*. At the conclusion of the electrolysis the transport number apparatus is removed from the thermostat and about as much liquid as would fill each limb gently run off, weighed and analysed. The weight of metal deposited in the coulometer is also determined. The transport numbers are then

calculated in the manner shown below for the determination of the transport numbers of the silver and nitrate ions.

Suppose that the silver content of a silver nitrate solution was determined by titration with N/10 potassium thiocyanate solution. A silver coulometer and the transport number apparatus were filled with this solution. The silver coulometer contained 100 g of electrolyte and initially it was found that this weight of solution required x ml of potassium thiocyanate solution for titration; after electrolysis, however, only y ml of the thiocyanate were required; the amount of current passed is therefore proportional to $(x - y)$. After electrolysis the anolyte (the solution in the anode

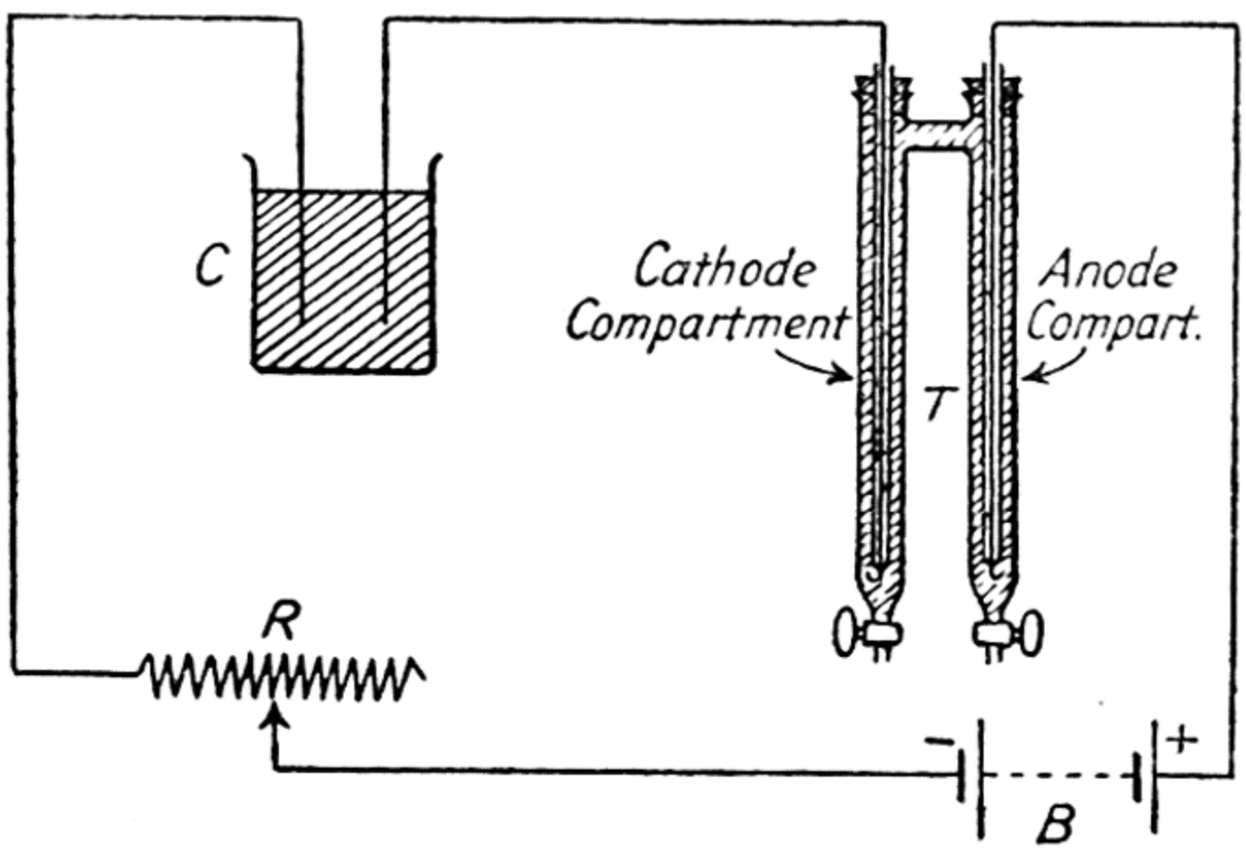


FIG. 101. Circuit Employed for the Determination of Transport Numbers

compartment) weighed a g and was found to require z ml of potassium thiocyanate solution. Silver in amount proportional to $(x - y)$ ml of N/10 potassium thiocyanate has, however, been dissolved from the anode of the transport number apparatus during the electrolysis. Therefore, the amount of the original silver nitrate remaining in the anolyte is proportional to $z - (x - y)$. Since 100 g of the silver nitrate solution initially required x ml of N/10 potassium thiocyanate solution for titration, then a g of silver nitrate would initially have required $ax/100$ ml of potassium thiocyanate solution. Therefore, the loss of silver from the anolyte is proportional to $(ax/100) - z - (x - y)$ ml of N/10 potassium thiocyanate solution. Thus, the transport number for the cation (that is for silver) is, from (19)—

$$\frac{(ax/100) - z - (x - y)}{(x - y)}$$

The values for transport numbers vary with the concentration of the electrolyte and with temperature. Some typical values are quoted in Table 51.

TABLE 51

Typical Transport Numbers for Cations at 18°*C*
(*after Glasstone*)

Electrolyte	Concentration (Gramme equivalents per litre)					
	0·005	0·02	0·05	0·10	0·20	0·50
NaCl . . .	0·397	0·396	0·393	0·390	0·385	0·374
KCl . . .	0·496	0·496	0·496	0·495	0·494	0·492
HCl . . .	0·832	0·833	0·834	0·835	0·837	0·838
$CdCl_2$ . . .	0·438	0·422	0·411	0·402	0·393	
CdI_2 . . .	0·445	0·442	0·396	0·296	0·127	0·003
$CuSO_4$ . . .		0·375	0·375	0·373	0·361	0·327

The variations in the values of transport numbers as quoted in Table 51 are probably due to various causes including the formation of complex ions, ionic hydration, and interionic attraction.

The Absolute Velocities of Ions. It should be noted that the ionic mobilities (i.e. ion conductances, *see* p. 255) are not the absolute velocities of the ions. The absolute velocities of ions are quoted in cm/sec under the influence of a potential different of 1 volt.

Consider a dilute solution to be contained between two flat, parallel electrodes each of which has an area of 1 cm^2, and separated by a distance of 1 cm, and to these two electrodes an e.m.f. of 1 volt is applied. If the velocity of the cations is u cm/sec, and that of the anions v cm/sec, then all the cations within the distance u cm will travel to the cathode in one second, whilst all the anions within the distance v cm will migrate in the opposite direction to the anode. If the concentration of the solution is c gramme equivalent/litre (i.e. c/1000 g. equivalent/ml) then in one second there will be transported a total of $c(u + v)$/1000 g. equivalent of cations and anions. Since each gramme equivalent of any ion carries a charge of one Faraday (i.e. 96 500 coulombs), then the total quantity Q of electricity carried per second is given by—

$$Q = \frac{96\,500c(u + v)}{1000} \text{ coulombs} \quad . \quad . \quad . \quad (23)$$

Now the conductance of a centimetre cube is equal, by definition, to the specific conductance k. In addition, by equation (11)—

$$\Lambda = \frac{1000\kappa}{c}$$

where Λ is the equivalent conductance, and c the concentration of

the solute in gramme equivalent/litre. Therefore, since the solution is dilute

$$\Lambda = \Lambda_0$$

and thus by equation (13)

$$\Lambda = \frac{1000\kappa}{c} = (l_+ + l_-)$$

and

$$\kappa = \frac{c(l_+ + l_-)}{1000} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

But by Ohm's Law—

$$I = \frac{E}{R} = E\kappa \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where I = current in amperes, E = applied e.m.f. in volts, R = specific resistance in ohms, and κ = specific conductance in reciprocal ohms.

Therefore, since the applied e.m.f. is 1 volt,

$$I = \frac{c(l_+ + l_-)}{1000}$$

Thus, the number of coulombs Q passing through one centimetre cube every second is

$$Q = \frac{c(l_+ + l_-)}{1000} \text{ coulombs} \quad . \quad . \quad . \quad . \quad (26)$$

and combining equations (23) and (26),

$$\frac{96\,500c(u + v)}{1000} = \frac{c(l_+ + l_-)}{1000}$$

Therefore, $$96\,500\,(u + v) = (l_+ + l_-)$$

and, from equation (14)—

$$96\,500u + 96\,500v = l_+ + l_-$$

Thus, $$96\,500u = l_+$$

and $$96\,500v = l_-$$

from which, $$u = l_+/96\,500$$

and, $$v = l_-/96\,500$$

Expressed in words, the absolute velocity in cm/sec of any ion under a potential difference of 1 volt/cm is obtained by dividing the ion conductance (in reciprocal ohms) by the Faraday (96 500 coulombs). Some typical results are given in Table 52.

TABLE 52

Ionic Velocities at 18°C for a Potential Difference of 1 volt/cm

Ion	Velocity (cm/sec)
Hydrogen	$32{\cdot}4 \times 10^{-4}$
Potassium	$6{\cdot}6 \times 10^{-4}$
Barium	$5{\cdot}7 \times 10^{-4}$
Sodium	$4{\cdot}5 \times 10^{-4}$
Hydroxyl	$18{\cdot}0 \times 10^{-4}$
Sulphate	$7{\cdot}0 \times 10^{-4}$
Chloride	$6{\cdot}8 \times 10^{-4}$
Nitrate	$6{\cdot}4 \times 10^{-4}$

A number of experimental determinations of ionic speeds have been made. Lodge (1896) used a U-tube which he filled with an agar-agar gel

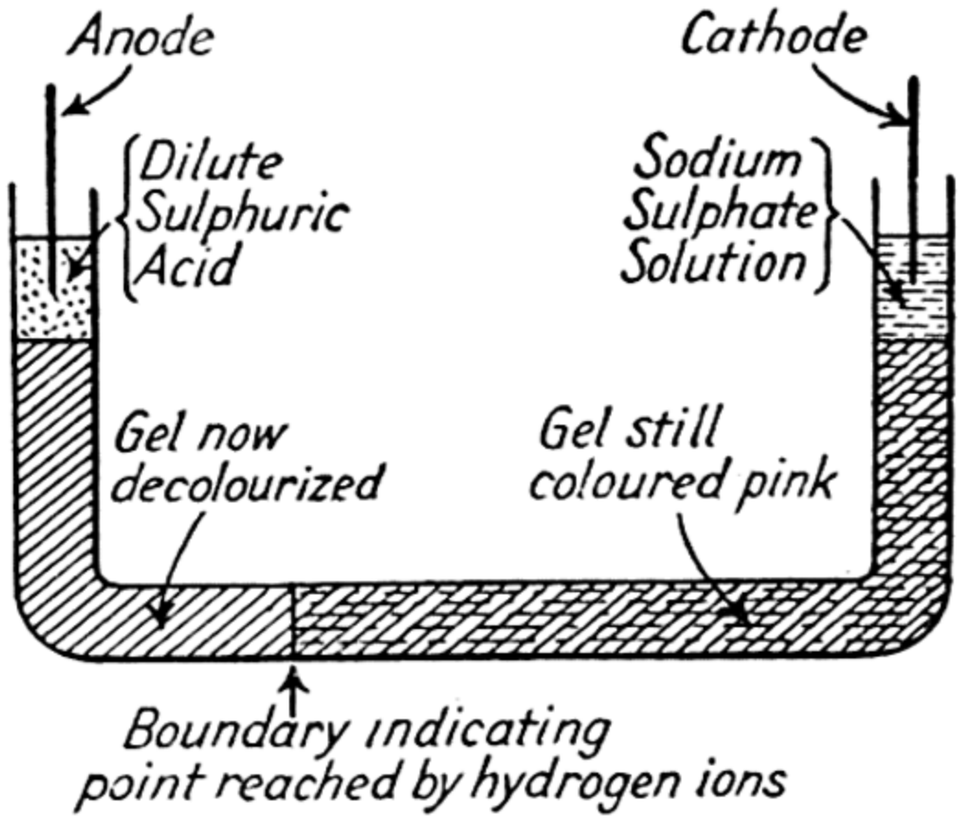


FIG. 102. Lodge's Apparatus for the Determination of Ionic Velocities

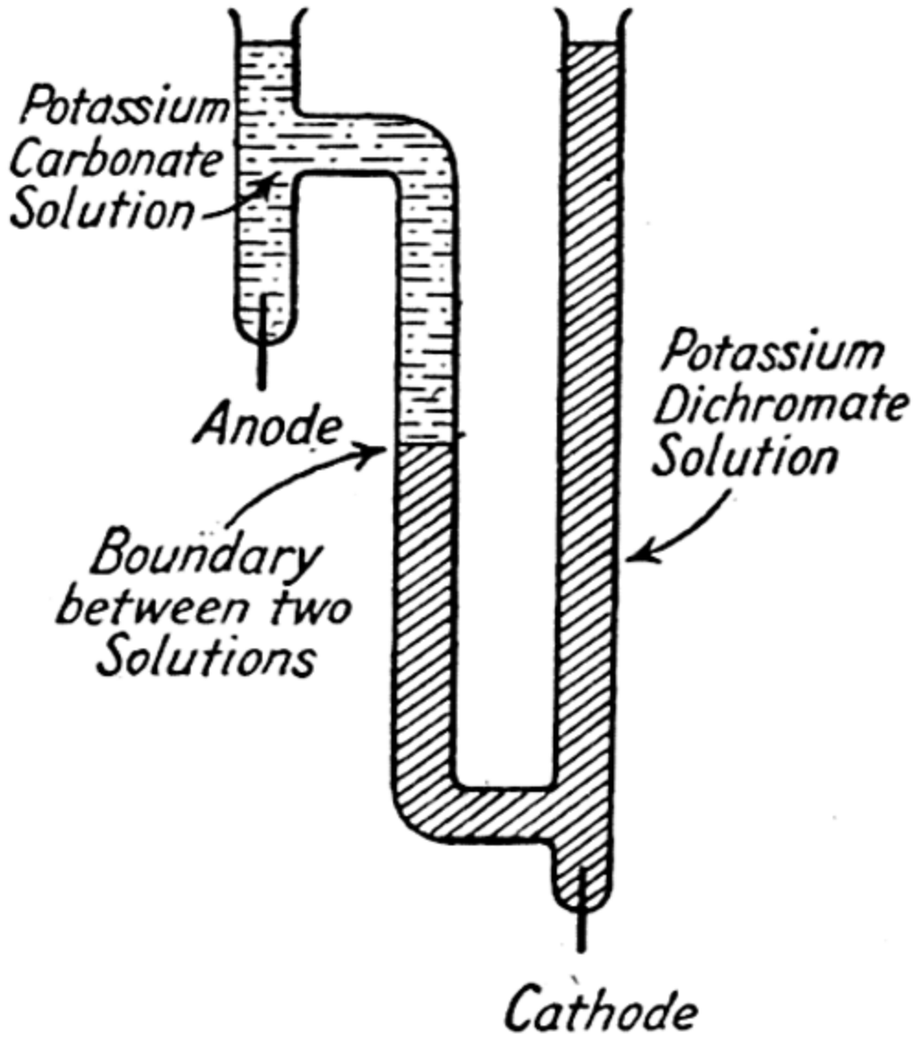


FIG. 103. Whetham's Apparatus for the Determination of Ionic Velocities

containing sodium chloride to serve as a conductor and phenolphthalein just turned pink by the addition of a trace of alkali (*see* Fig. 102). When the gel had set, a small quantity of dilute sulphuric acid was added to one side of the U-tube and a little sodium sulphate solution to the other; platinum electrodes were then placed in each limb, the electrode immersed in the sulphuric acid being made the anode and that immersed in the sodium sulphate solution the cathode. On connecting the electrodes to a d.c.

supply, the hydrogen ions migrated through the gel, their progress being indicated by the progressive decolorizing of the phenolphthalein.

Another technique, introduced by Whetham (1893), involves the use of two solutions of almost the same conductance and having one ion in common. One such pair of substances is potassium dichromate and potassium carbonate. If an apparatus such as that shown in Fig. 103 is used, the coloured Cr_2O_7'' ion moves, and its progress may be followed by noting the position of the boundary.

ELECTRODE POTENTIALS AND THE E.M.F.s OF GALVANIC CELLS

When a metal is placed in a solution of one of its salts, equilibrium is attainable between the metal and the solution only by movement of metal ions. Thus when a metal dips into a solution containing its ions it will exhibit a tendency to pass into the solution as positive ions. This property, which is non-variable, possessed by hydrogen as well as by the metals, was termed *solution pressure* by Nernst (1889). With the noble metals, gold, silver, platinum, etc., the solution pressure is very low, but in the case of reactive metals such as the alkali metals, it is high. Hydrogen and each of the metals all have a characteristic solution pressure which may be regarded as a measure of their readiness to pass as positive ions into solution.

Electrode Potentials. The loss of positive ions leaves the metal electrode negatively-charged and the accumulation of electrons on the metal surface results in the establishment of an electrostatic field or "electrical double layer" which tends to hold the positive metal ions in the solution close to the metal electrode surface. This process of ion formation does not normally continue indefinitely, in fact a state of equilibrium is rapidly attained; actually only a minute amount of metal passes into solution as positive ions.

The potential across the metal-solution interface is dependent upon the metal ion concentration of the solution, that is, upon the osmotic pressure of the solution. Thus, if the concentration of metal ions in the solution is increased by adding more of the metal salt, the effect of the increased osmotic pressure which results is to drive back some of the positive metal ions on to the metal electrode with the consequent reduction of the potential difference across the metal-solution interface. Metal ions will therefore continue to pass from the electrode to the solution until this tendency is just counterbalanced by the tendency for positive ions to be deposited from the solution on to the metal electrode; in other words, until the solution pressure is just counterbalanced by the osmotic pressure. According as to whether the solution pressure is greater than, equal to, or less than the osmotic pressure, so the potential and the sign of the charge on the metal electrode will vary. If the solution pressure P is greater than

the osmotic pressure p (e.g. zinc) then positive ions will pass into the solution and the metal electrode will acquire a negative charge (*see* Fig. 104 (*A*)). When P and p are equal, then no ions will pass into the solution, nor will any ions pass from the solution to the electrode with the result that the metal electrode will not develop any potential (*see* Fig. 104 (*B*)). On the other hand, if P is less than p, as is the case with copper, gold, silver and platinum, then positive metal ions will pass from the solution to the metal with the result that the electrode will acquire a positive charge (*see* Fig. 104 (*C*)).

The potential difference between a metal and a solution of its ions (in equilibrium) is known as the *electrode potential* of that metal. The electrode

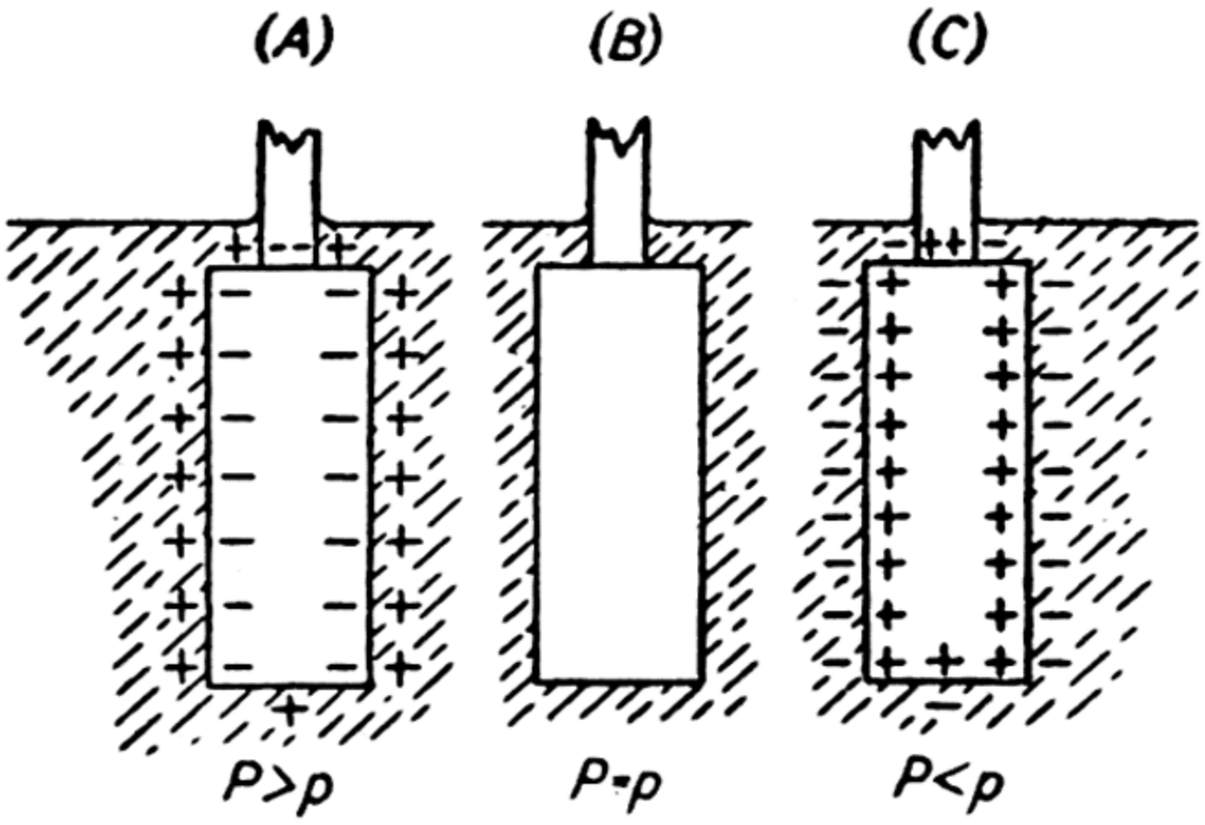


FIG. 104. Development of Electrode Potential

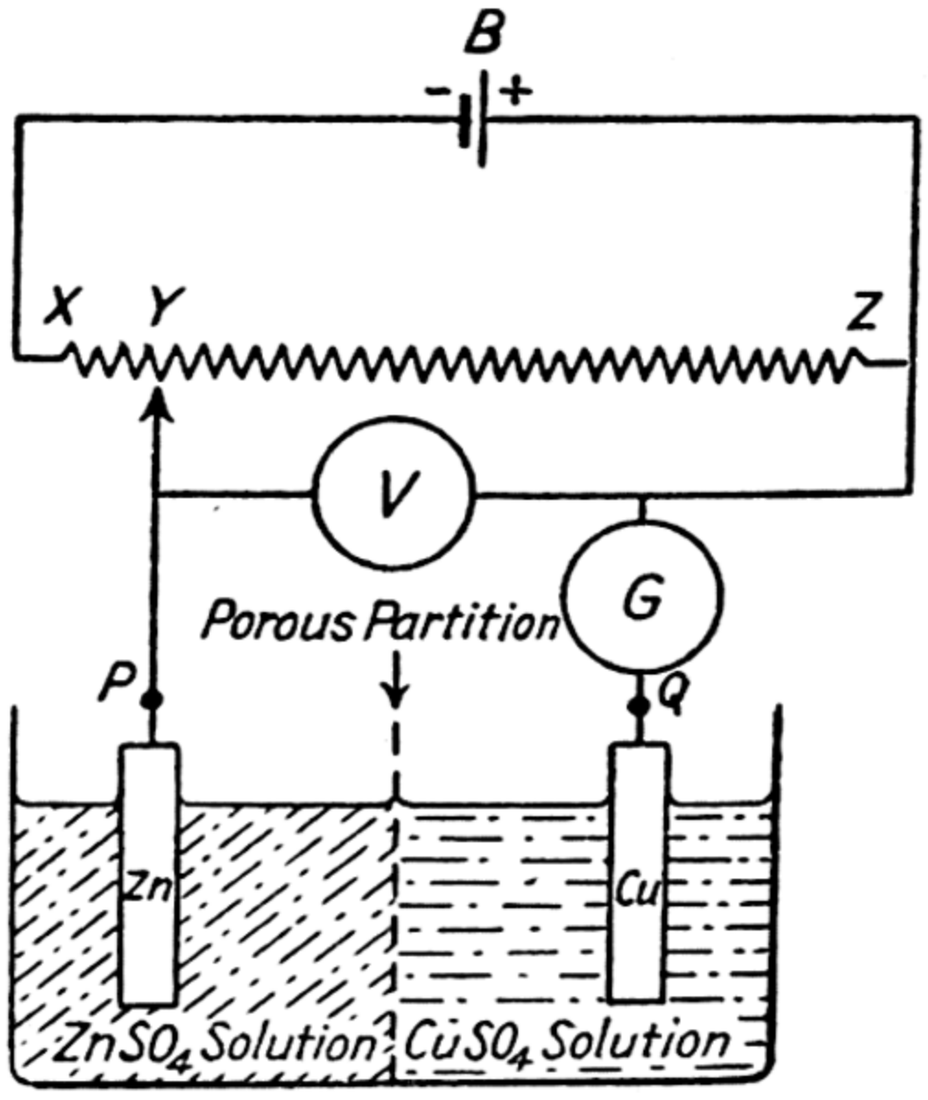


FIG. 105. Daniell Cell and Simple Potentiometer

potential of a metal is dependent, amongst other factors, upon the physical state of the metal, the temperature and, as stated above, upon the concentration of metal ions in the solution.

If two different metals (e.g. zinc and copper) are each placed individually in solutions of their salts, the two solutions being separated by a porous partition (*see* Fig. 105), it is possible by means of a potentiometer to measure the e.m.f. of the *galvanic cell* thus set up. In this circuit the potentiometer XYZ is supplied with current by the battery B. The two metal electrodes are connected as shown in Fig. 105, and the movable contact Y moved along the slide wire XZ until the galvanometer G gives no deflection. This condition indicates that the e.m.f. of the galvanic cell is exactly equal to the potential difference between the points Y and Z which may be read off at once from the voltmeter V. This e.m.f. however is the combined e.m.f. of two single electrode potentials for the metals

zinc and copper making up the cell and it is impossible to state from the value of e.m.f. measured what proportion is due either to the zinc, or to the copper.

If it is desired to measure the single electrode potential for a metal electrode it is necessary to combine that electrode with a standard electrode of known potential difference. The standard electrode usually adopted is the hydrogen electrode which consists of a strip of platinum foil, coated with platinum black, partially immersed in an acid solution containing hydrogen ions at a concentration of one gramme ion per litre, that is, a

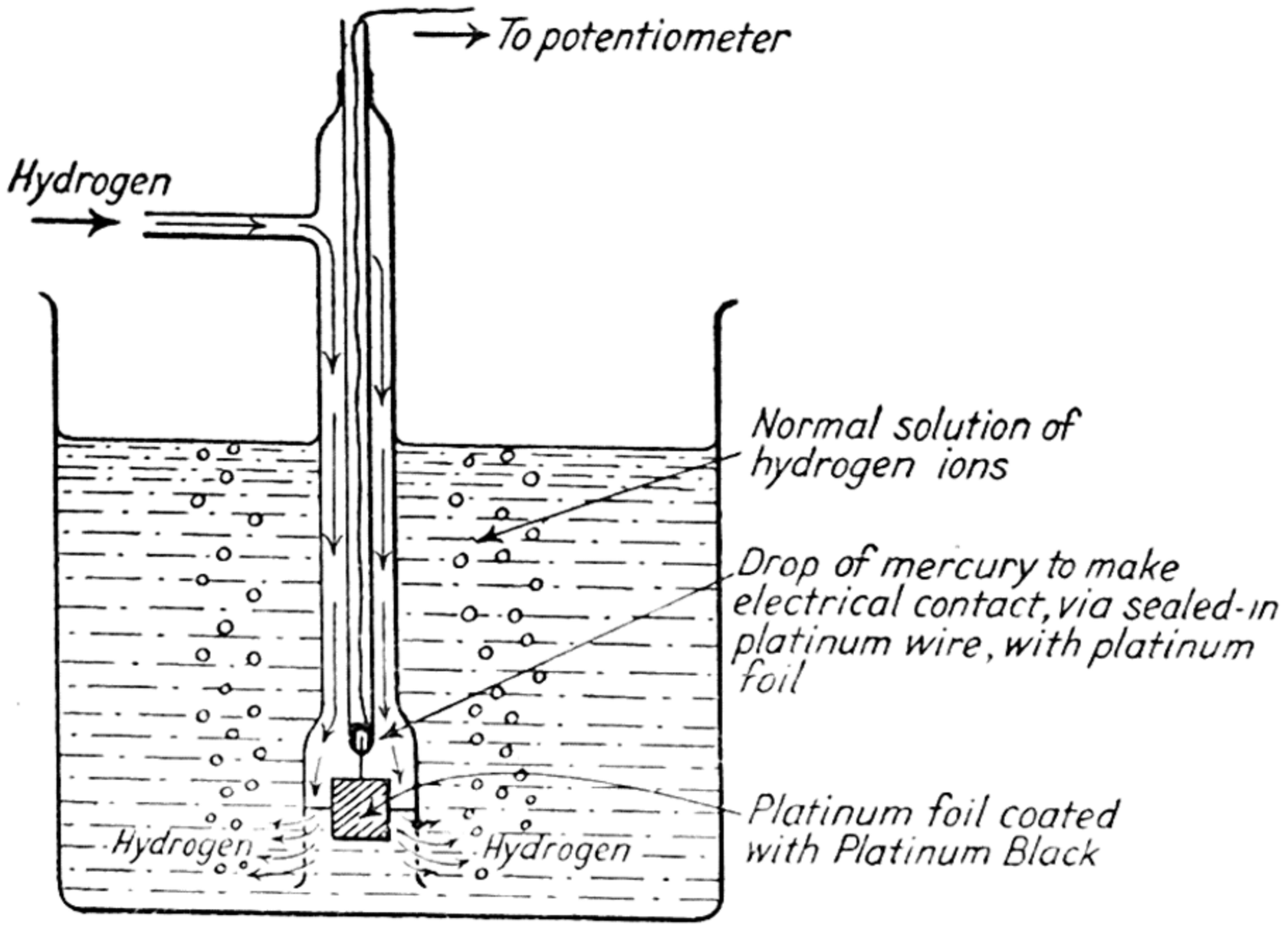


FIG. 106. Hydrogen Electrode

normal solution, and kept continuously saturated with hydrogen gas at one atmosphere pressure. This is the so-called *normal hydrogen electrode.* There are many forms of hydrogen electrodes but one typical form is shown in Fig. 106.

The hydrogen electrode is considered arbitrarily to be at zero potential at all temperatures, and electrode potentials determined against this standard are termed electrode potentials on the hydrogen scale.

The hydrogen electrode is very reproducible, but it is not easily set up; hence a secondary standard electrode which is more convenient to use for ordinary purposes than the hydrogen electrode is generally employed. This is the *calomel electrode*, which consists of mercury in contact with a solution of potassium chloride saturated with mercurous chloride, Hg_2Cl_2 (calomel). The title "calomel electrode" is usually preceded by the concentration of the potassium chloride solution; thus, for example, one may use the 0·1N, the 1·0N, and the saturated calomel electrodes. One form

of the calomel electrode is shown in Fig. 107; electrical connexion with the mercury at the bottom of the cell is made by means of a piece of platinum wire which is sealed in the end of the glass tube dipping into the cell.

The Daniell cell, as shown in Fig. 105, may be regarded as being made

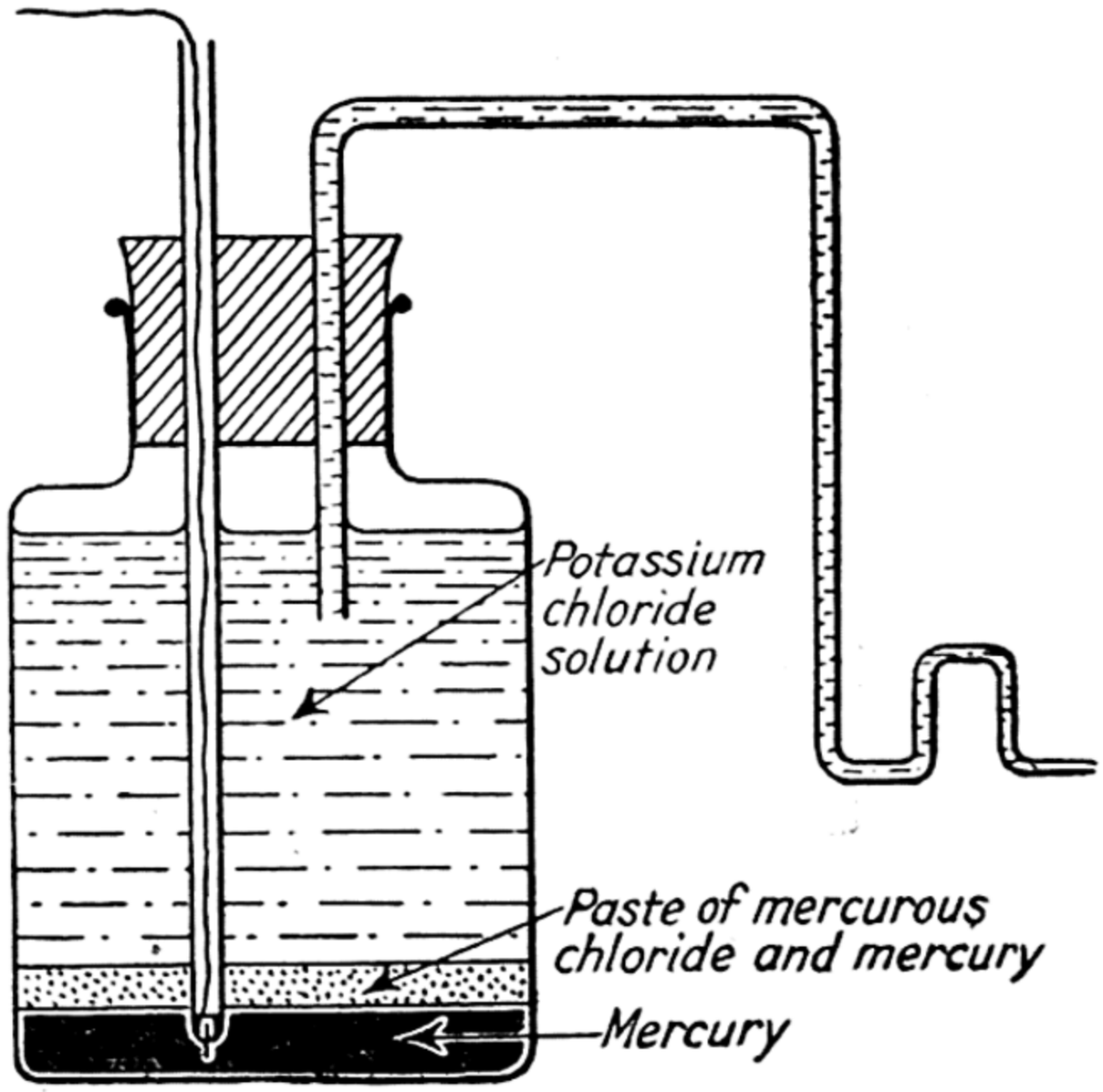


FIG. 107. Calomel Electrode

up of two "half-cells," in fact any such cell may be regarded as being made up of two half-cells—

$M_1 \mid M_1$ salt solution

and $M_2 \mid M_2$ salt solution

Similarly, the hydrogen electrode and the calomel electrode are also half-cells.

If the hydrogen electrode and the calomel electrode are arranged in circuit as shown in Fig. 108, the e.m.f. of the calomel cell *on the hydrogen scale* may be determined by means of a potentiometer on connecting the two contacts R and S (Fig. 108) to the two terminals, P and Q (Fig. 105), after disconnecting the Daniell cell as shown in Fig. 105. The hydrogen electrode dips into a 1·2N hydrochloric acid solution (1·2N hydrochloric acid has a normal hydrogen ion activity) which is brought into circuit with the potassium chloride of the calomel cell C by means of an intermediary bridge of a concentrated solution of a salt such as potassium chloride or ammonium nitrate. Since both of these salts give ions which have almost the same mobility the potential difference at the junction of the two salt solutions is very low and thus errors may be minimized. This concentrated salt solution contained in the beaker B is often called a "salt bridge."

The potentials of the three types of calomel cell are thus determined to be—

0·1N KCl Calomel electrode + 0·334 volt
1·0N KCl Calomel electrode + 0·281 volt
Saturated KCl Calomel electrode + 0·242 volt

The simple type of potentiometer as shown in Fig. 105 is, of course, only suitable for rough measurements. For precise work it is customary

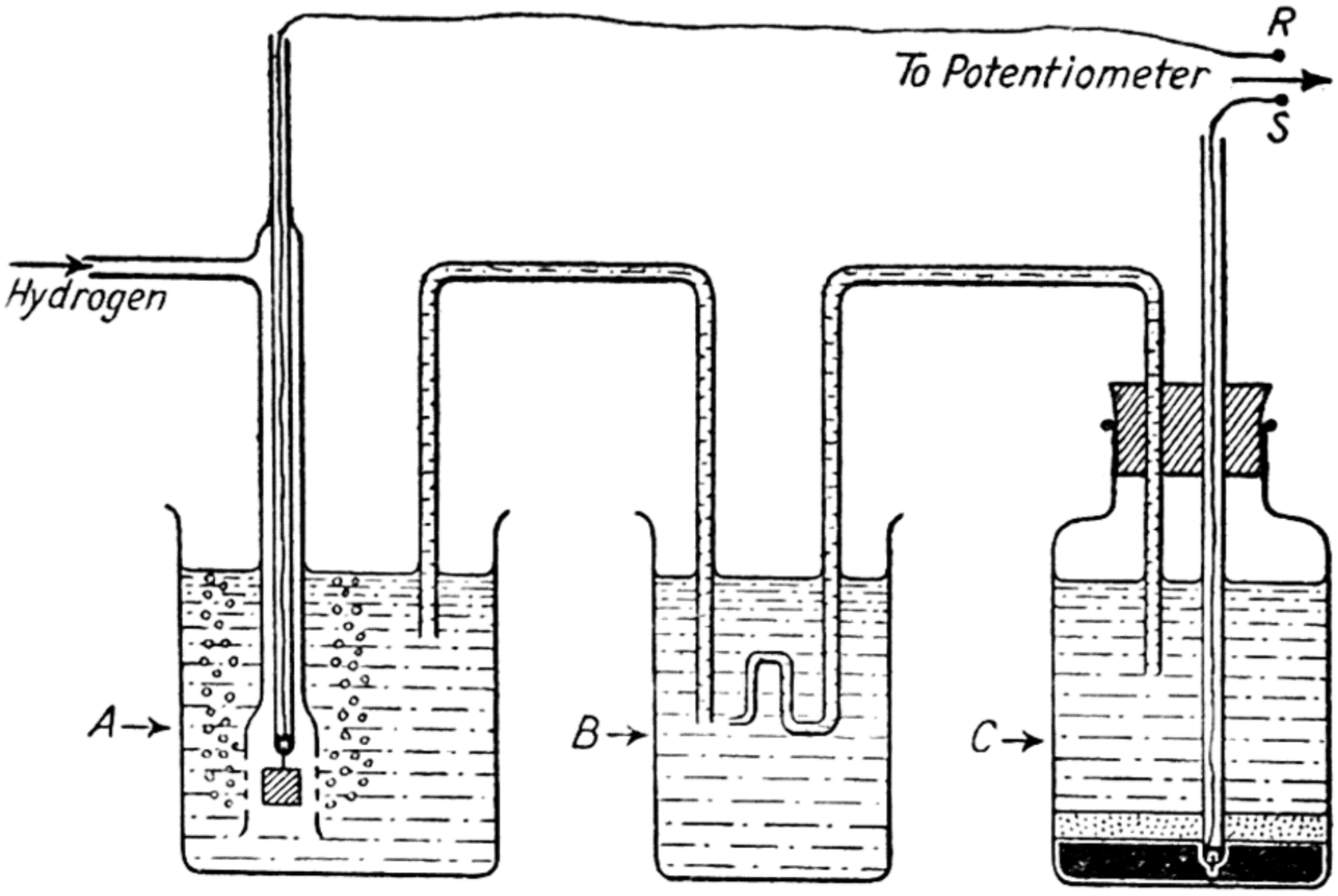


FIG. 108. Arrangement of Apparatus for the Determination of the e.m.f. of the Calomel Cell

to employ a potentiometer having its resistance coils calibrated in terms of the e.m.f. applied to its output terminals. In addition, a standard cell (e.g. a Weston cell) is usually incorporated so as to permit of the potentiometer being standardized prior to making observations with the output from two half-cells connected to the instrument.

If it is desired to determine the electrode potential of a metal, it is only necessary to immerse a specimen of the metal in question in a normal solution of one of its salts, as shown in Fig. 109, and then to connect it to a normal hydrogen electrode via the connecting solution, instead of to a calomel electrode as shown in Fig. 108. Thus the wire *T* (Fig. 109) takes the place of the wire *S* (Fig. 108). Alternatively, it is often more convenient to connect the metal electrode, again through the connecting solution, to the calomel electrode in which case the wire *T* (Fig. 109) takes the place of the wire *R* (Fig. 108). Suppose that it is desired to determine the electrode potential of silver; a piece of the metal is immersed in normal solution of silver nitrate and connected through a salt bridge, say

ammonium nitrate in this case, to a calomel electrode. The combination may be depicted as follows—

$$\text{Hg} \;\Big|\; \begin{matrix}\text{Hg}_2\text{Cl}_2\\ \text{(Normal KCl)}\end{matrix} \;\Big|\; \begin{matrix}\text{Connecting solution}\\ \text{(e.g. } \text{NH}_4\text{NO}_3\text{)}\end{matrix} \;\Big|\; \begin{matrix}\text{AgNO}_3\\ \text{(Normal solution)}\end{matrix} \;\Big|\; \text{Ag}$$

The potential of this combination is then measured by means of a potentiometer.

Since the potential of the calomel electrode is positive to the hydrogen electrode, the appropriate value for the calomel electrode must be added to the potential derived from the above combination. Thus, if the potential of the combination was found to be + 0·518 volt, and if a 1·0N KCl calomel electrode was employed, that is, with a potential of + 0·281 volt on the normal hydrogen scale, then the single electrode potential for silver is—

$$0{\cdot}518 + 0{\cdot}281 = + 0{\cdot}799 \text{ volt}$$

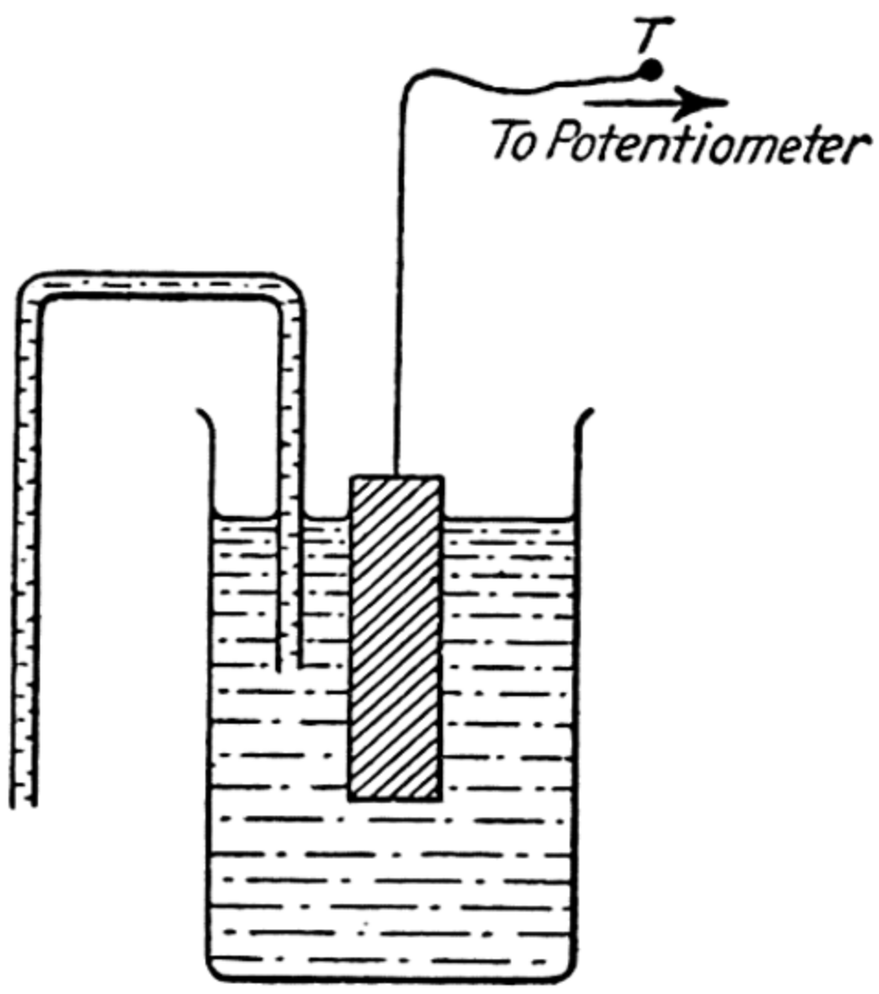


FIG. 109. Determination of the Electrode Potential of a Metal

It should be noted that the silver has a potential which is positive to the calomel electrode and this is the reason for *adding together* the potentiometer value and the calomel electrode potential. In the case of base metals, however, it is found that they give a potential which is negative to the calomel electrode so that the algebraic sum of the potentiometer value and the calomel electrode potential in such cases results in a *decrease* in the numerical value of the electrode potential for the base metal concerned. The values of some standard electrode potentials on the hydrogen scale are given in Table 53.

From Table 53 it will be observed that the noble metals are placed at the positive end of the table, whilst the more active metals appear at the negative end of the table. This sequence is known as the *electrochemical series*; the order in which the metals appear in this series also gives the order of replaceability. Thus, a metal will be displaced from a solution of one of its salts provided that the displaced metal is more positive than the metal acting as displacer. Such displacement occurs most readily when a pair of metals is widely spaced in the electrochemical series. Thus, zinc will displace nickel from solution, iron will displace copper, and copper will displace silver. The position of hydrogen in the electrochemical series is important; the metals which are positive to hydrogen (e.g. gold, silver and platinum, etc.) will not normally displace hydrogen from acids, whilst metals which are negative to hydrogen (e.g. tin, iron, zinc and

aluminium, etc.) will do so with increasing ability as they become more negative. In fact, the very reactive alkali metals are able to liberate hydrogen from water in which the concentration of hydrogen ions is very small.

TABLE 53

Standard Electrode Potentials at 25°C
(*after U. R. Evans*)

Metal	Ion Concerned	Normal Electrode Potential on the Normal Hydrogen Scale
		(volts)
"*Base*" *end*—		
Lithium*	Li^+	− 3·02
Potassium*	K^+	− 2·922
Sodium*	Na^+	− 2·712
Magnesium*	Mg^{++}	− 2·375
Aluminium*	Al^{+++}	− 1·67
Zinc	Zn^{++}	− 0·762
Chromium	Cr^{++}	− 0·71
Iron	Fe^{++}	− 0·44
Cadmium	Cd^{++}	− 0·402
Nickel	Ni^{++}	− 0·250
Tin	Sn^{++}	− 0·136
Lead	Pb^{++}	− 0·126
Hydrogen (1 atmosphere)	H^+	0·000
Copper	Cu^{++}	+ 0·3448
Mercury	$(Hg_2)^{++}$	+ 0·7986
Silver	Ag^+	+ 0·7995
Platinum	Pt^{++}	+ 1·2 (approx)
Gold	Au^{+++}	+ 1·42
"*Noble*" *end*—		

* These are calculated values, and of theoretical interest only. Aluminium, unless amalgamated, gives nobler values, owing to the presence of an oxide film. The other metals evolve hydrogen freely, and potential measurements made directly would not represent equilibrium values.

The Variation with Concentration of Electrode Potential

The potential of the normal hydrogen electrode is dependent upon the maintenance of (*a*) a steady concentration of molecular hydrogen at a pressure of one atmosphere, and (*b*) a steady concentration of hydrogen

ions at unit activity in the electrolyte. If either, or both of these factors vary the potential of the hydrogen electrode will also vary. Similarly, the potential of a metal electrode varies as the concentration of metal ions in the electrolyte varies.

The laws underlying the variations of both these types of electrodes are made clear by a consideration of what is termed a "concentration cell." A concentration cell, which is shown diagrammatically in Fig. 110, consists essentially of two electrodes of the same metal immersed in solutions of the same salt of this metal at two different concentrations which here will be termed C_1 and C_2. Let the valency of the

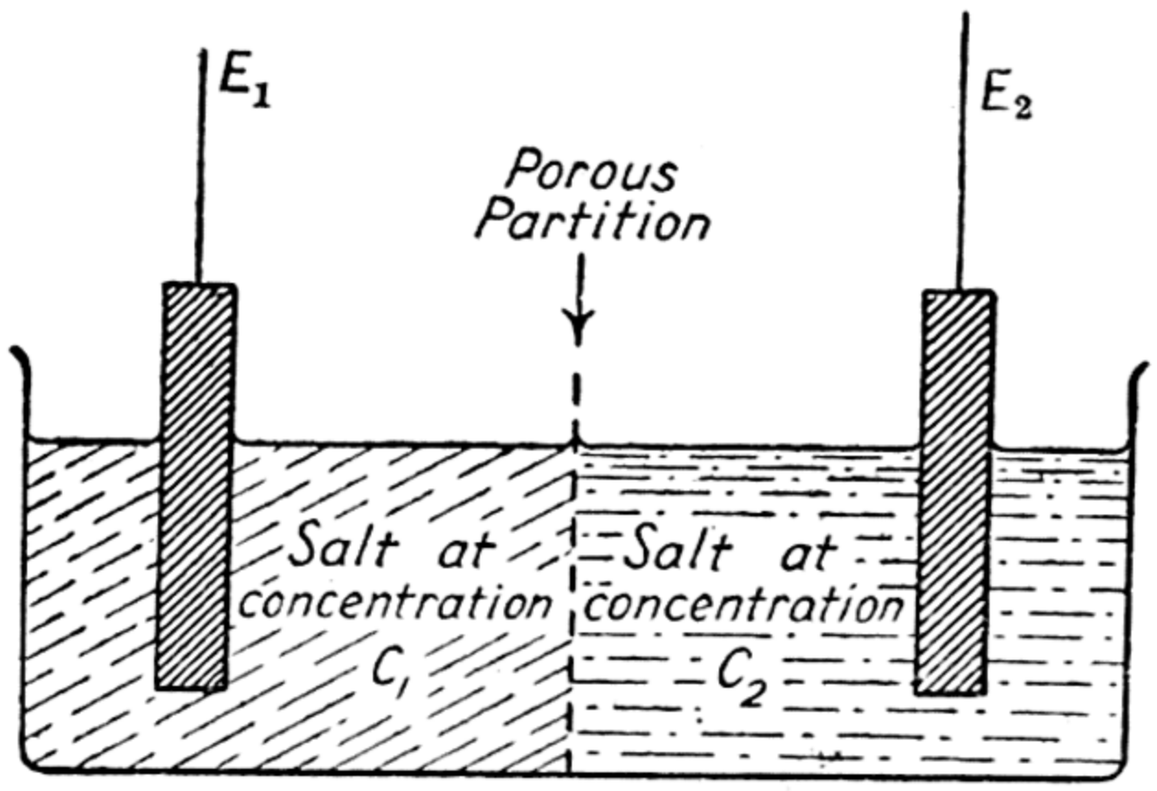


FIG. 110. Concentration Cell

cation be n and the potentials of the two electrodes be E_1 and E_2 respectively.

If one gramme equivalent of the metal is dissolved from one electrode and deposited on the other electrode then the charge Q which has passed through the concentration cell is given by—

$$Q = nF \text{ coulombs}$$

where, $F = 1$ faraday

Since the potential difference between the two electrodes is $E_1 - E_2$, and assuming that $E_1 > E_2$, then the electrical work W which has been done is

$$W = nF(E_1 - E_2) \quad . \quad . \quad . \quad . \quad (27)$$

assuming that there is no potential difference at the partition.

Now the process of transferring one gramme equivalent of the metal from one electrode to the other, that is, from one concentration to another concentration, may be considered as being done by an isothermal and reversible expansion, doing work against the osmotic pressure. Thus,

assuming that the ions obey the gas laws, and that p represents the osmotic pressure of the ions then the work done—

$$W = \int_{v_1}^{v_2} p\,dv$$

where the dilutions, v_1 and v_2, are the reciprocals of C_1 and C_2 respectively.

Therefore
$$W = \int_{v_1}^{v_2} \frac{RT}{v}\,dv$$
$$= RT \log_e \frac{v_2}{v_1}$$
$$= RT \log_e \frac{C_1}{C_2} \quad . \quad . \quad . \quad . \quad (28)$$

where R = gas constant, T = absolute temperature.

Equating the two work terms, (27) and (28)

$$nF(E_1 - E_2) = RT \log_e \frac{C_1}{C_2}$$

so that
$$E_1 - E_2 = \frac{RT}{nF} \log_e \frac{C_1}{C_2}$$
$$= \frac{2{\cdot}303RT}{nF} \log_{10} \frac{C_1}{C_2} \quad . \quad . \quad (29)$$

Introducing values for R and F and taking the temperature to be 18°C, the factor

$$\frac{2{\cdot}303RT}{F} = 0{\cdot}058 \text{ volt}$$

At 25°C, the same factor $= 0{\cdot}0591$ volt

Thus, at 18°C, (29) may be simplified to—

$$E_1 - E_2 = \frac{0{\cdot}058}{n} \log_{10} \frac{C_1}{C_2} \quad . \quad . \quad . \quad . \quad (30)$$

or,
$$E_1 = E_2 + \frac{0{\cdot}058}{n} \log_{10} \frac{C_1}{C_2} \quad . \quad . \quad . \quad (31)$$

Now if the standard electrode potential of a metal be the e.m.f. designated by E_2, the solution in which this electrode is immersed must have the concentration $C_2 = 1$.

Therefore
$$E_1 = E_{\text{-}} + \frac{0{\cdot}058}{n} \log_{10} C_1 \quad . \quad . \quad . \quad . \quad (32)$$

or, as is customary, designating the standard electrode potential by the symbol E_0—

$$E_1 = E_0 + \frac{0{\cdot}058}{n} \log_{10} C_1 \quad . \quad . \quad . \quad (32a)$$

The relationship (32*a*) derived above refers only to the condition of equilibrium existing between an electrode and positively-charged ions in solution (i.e. cations). It may, however, be applied to the equilibrium conditions existing between an anode and anions, in which case it is only necessary to change the sign, thus—

$$E_1 = E_0 - \frac{0{\cdot}058}{n} \log_{10} C_1 \quad . \quad . \quad . \quad (32b)$$

Equations (32*a*) and (32*b*) are forms of the Nernst equation.

From a consideration of (32*a*) it will be noted that a ten-fold increase of concentration varies the electrode potential by $0{\cdot}058/n$ volts at 18°C. Likewise, for anions a similar increase of concentration decreases the electrode potential by $0{\cdot}058/n$ volt at 18°C.

Reconsidering equation (31) it is possible to select a metal ion concentration C_1 which is such that the osmotic pressure which it exerts will just balance the solution pressure of the metal; similarly, for concentration C_2 of metal ions in the electrolyte the osmotic pressure may be substituted. Thus the quotient C_1/C_2 in (31) is proportional to solution pressure/osmotic pressure. Therefore, in the case of metals such as zinc, for which solution pressure is greater than osmotic pressure, the numerical value of the quotient, C_1/C_2, and therefore E_1, is *increased by diminishing the concentration of zinc ions*, that is, the osmotic pressure. In the case of metals like copper, however for which the solution pressure is less than the osmotic pressure, the numerical value of C_1/C_2 and therefore the electrode potential is *decreased by diminishing the concentration of metal ions*. Summarizing—

If ions are discharging at the electrode (e.g. copper)	Reduction in ionic concentration leads to e.m.f. reduction Increase in ionic concentration leads to e.m.f. increase
If new ions are being formed at the electrode (e.g. zinc)	Reduction in ionic concentration leads to e.m.f. increase Increase in ionic concentration leads to e.m.f. reduction

A consideration of the behaviour of the Daniell cell under varying conditions is of assistance in understanding more clearly the principles stated above. In the Daniell cell, when the copper and the zinc plate are connected, the cell e.m.f. is initially the algebraic sum of the electrode potentials for copper and zinc respectively. Since the salt solutions are

not normal solutions these values are of the order of + 0·3 volt for copper, and − 0·8 volt for the zinc. The cell e.m.f. is therefore 1·1 volts (see Fig. 111). As a result of connecting the two electrodes together, the copper plate becomes less positive, whilst the zinc plate becomes progressively more positively charged, that is less negative. In order to restore equilibrium, copper ions are deposited on the copper plate whilst zinc ions pass from the zinc plate to the electrolyte. The supply of copper ions in the solution is, however, unlimited; and also the electrolyte ultimately becomes saturated in respect of zinc ions—as zinc sulphate—so that the concentration of zinc sulphate cannot increase beyond this value. The net result of these processes is that the copper plate and the zinc plate ultimately both attain the same potential, A' and C' (Fig. 111).

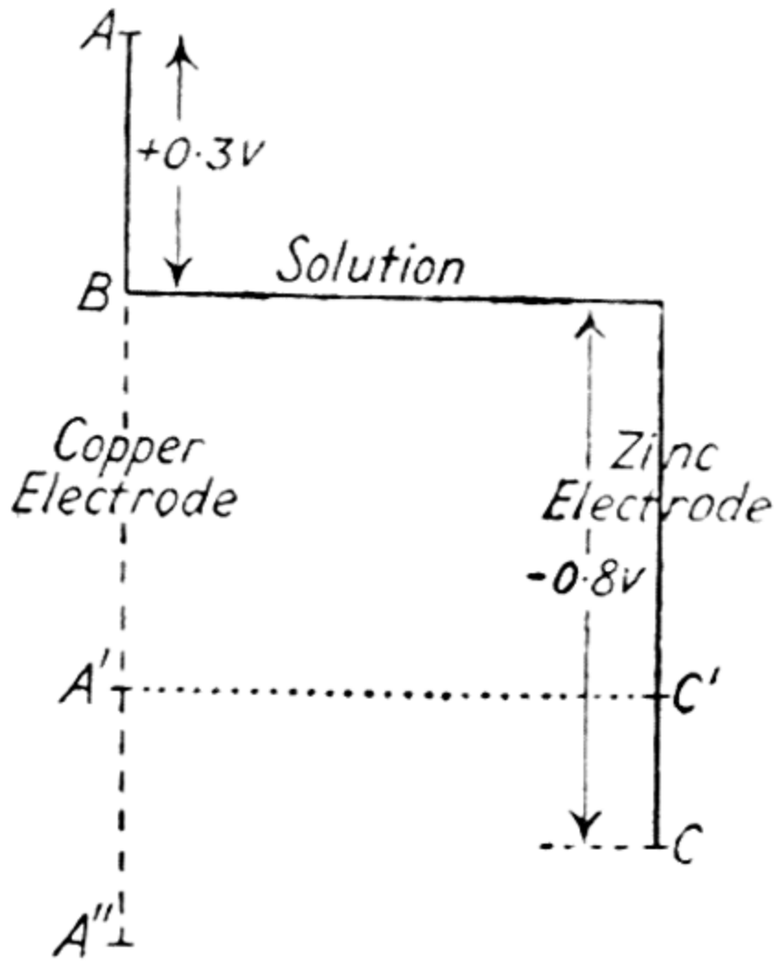


FIG. 111. Influence of Concentration Variation upon Cell e.m.f.

The reason for the copper electrode undergoing a far greater change of potential than the zinc electrode is that once the electrolyte has become saturated with zinc sulphate further change in potential of the zinc electrode is impossible. The concentration of the copper ions may however be decreased below that of the point A' to A'' by adding potassium cyanide solution to the copper salt solution when the copper ions are converted into the complex salt potassium cuprocyanide, $K_3[Cu(CN]_4]$; the net result is that the concentration of the copper ions is so extremely low that the polarity of the Daniell cell is reversed. In a concentration cell in which there are two similar and externally connected electrodes of potentials E_1 and E_2 respectively immersed in two differing concentrations of the same electrolyte, which are in contact with one another via a porous partition, the current will flow through the wire from E_1 to E_2 if C_1 is greater than C_2, whilst through the electrolyte the current flow is from the dilute to the more concentrated electrolyte.

Hydrogen Ion Concentrations. Hydrogen electrodes are often employed for determining the hydrogen ion concentration in aqueous solutions. The potential of the hydrogen electrode is usually measured by combining it with a standard electrode such as one of the calomel electrodes. If the 1·0N KCl calomel electrode is employed with an e.m.f. of + 0·281 volt on the hydrogen scale, the e.m.f. of the combination is—

$$H_2 \mid H^+ \mid 1{\cdot}0N\ KCl\ Hg_2Cl_2 \mid Hg$$

$\longleftarrow$ $0{\cdot}058 \log_{10} [H^+]$ (at 18°C)

$\longrightarrow$ 0·281 volt

Now, the potential, E, of the system, calomel electrode—solution—hydrogen electrode is—

$$E = E_{\text{Calomel}} - E_{\text{Hydrogen}} \quad . \quad . \quad . \quad . \quad (33)$$

the calomel electrode being positive.

Therefore, $$E = 0{\cdot}281 - 0{\cdot}058 \log_{10}[H^+]$$

and $$-0{\cdot}058 \log_{10}[H^+] = E - 0{\cdot}281$$

$$-\log_{10}[H^+] = \frac{E - 0{\cdot}281}{0{\cdot}058} \quad . \quad . \quad . \quad . \quad (34)$$

Now the quantity $-\log_{10}[H^+]$ is known as the p_H value of the solution, so that—

$$p_H = \frac{E - 0{\cdot}281}{0{\cdot}058} \quad . \quad . \quad . \quad . \quad (35)$$

The hydrogen electrode is very sensitive to the presence of alkaloids, ammonia, proteins, ions of the noble metals and oxidizing agents such as chromates. All these substances cause a progressive drift of the electrode potential towards a positive value, a phenomenon known as poisoning. In the absence of such poisons however, the hydrogen electrode is capable of giving accurate readings over the whole p_H range.

The Quinhydrone Electrode. When quinone is added to a solution containing hydrogen ions the following reversible reaction occurs—

$$\underset{\text{Quinone}}{C_6H_4O_2} + 2H^+ \rightleftharpoons \underset{\text{Hydroquinone}}{C_6H_6O_2} + 2e \quad . \quad . \quad . \quad (36)$$

If an electrode of bright platinum foil is immersed in the solution the electrons are taken up by the electrode, the potential of which is measured in the same way as for a hydrogen electrode using a calomel electrode to complete the circuit. By direct comparison with solutions of known p_H, the e.m.f. of the quinhydrone electrode is given by the following expression—

$$E = 0{\cdot}704 + 0{\cdot}058 \log_{10}[H^+] \quad . \quad . \quad . \quad (37)$$

From which

$$p_H = \frac{0{\cdot}704 - E_m - E_{cal}}{0{\cdot}058} \text{ (at 18°C)} \quad . \quad . \quad . \quad (38)$$

where E_m = e.m.f. measured on potentiometer

and E_{cal} = e.m.f. of calomel cell

The quinhydrone electrode, although not capable of such general application as the hydrogen electrode since it can be employed only in solutions of p_H lower than 8, is nevertheless easier to set up than the hydrogen electrode and, in addition, it does not require a supply of hydrogen.

The Glass Electrode. The fact that the potential difference between a glass surface and a solution varies with the p_H value of the latter is employed as a means of determining the p_H of a solution by means of the glass electrode. The glass electrode consists essentially of a thin-walled bulb made from a low melting point glass of high electrical conductivity (*see* Fig. 112 at *G*) in which is placed a solution *S* of known and constant p_H, together with a little quinhydrone and a platinum wire *P*, to make electrical connexion. In use, the glass electrode is placed in the solution under investigation *X*, and a calomel electrode *C* included to complete the circuit. Since the electrical resistance of the glass electrode is very high (10–100 megohms) a thermionic valve potentiometer must be employed to measure the e.m.f. of the cell. The glass electrode is standardized in three or four solutions of known p_H covering the range of hydrogen ion concentration under investigation and a calibration curve drawn connecting the e.m.f. of the cell with p_H. In actual use the p_H is read off from this calibration curve after measuring the e.m.f. of the cell. The glass electrode can be used in almost all solutions except those which are very acid or very alkaline.

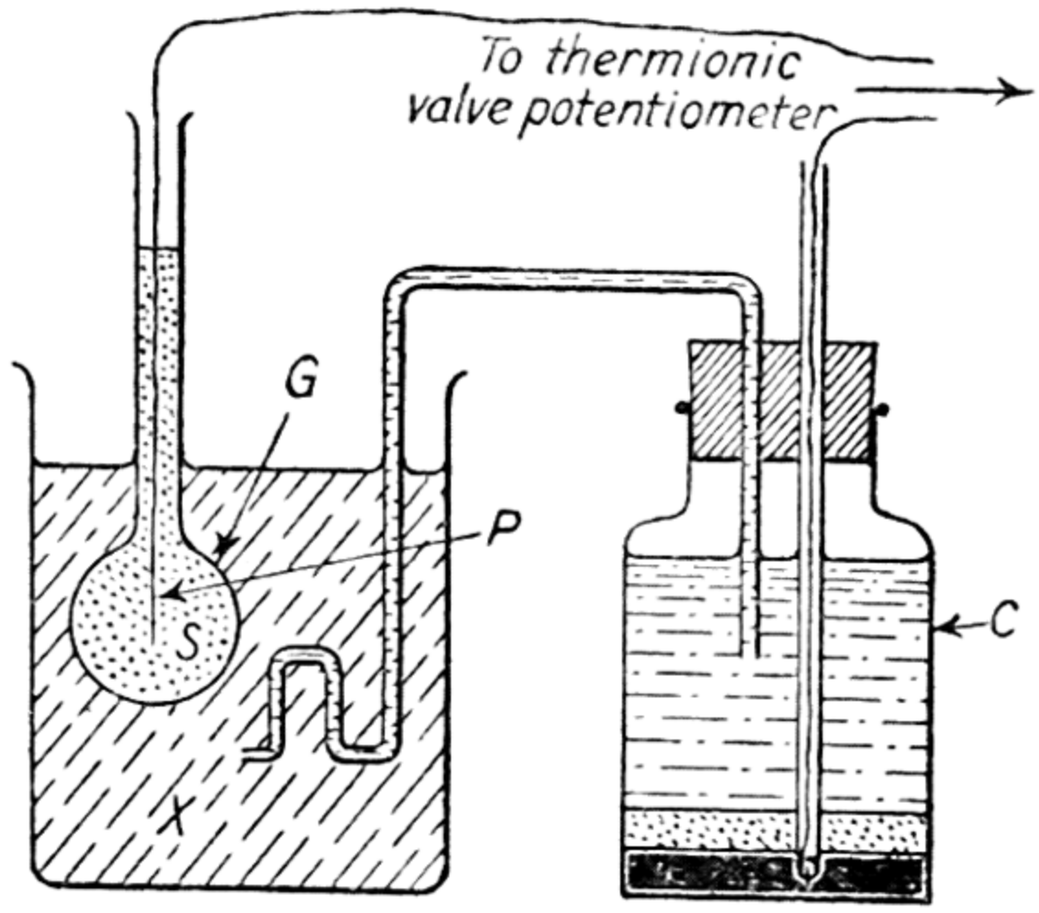


FIG. 112. Circuit Arrangement for Use of Glass Electrode

OXIDATION-REDUCTION POTENTIALS

The term *oxidation* is used in connexion with chemical reactions to imply the addition of oxygen, the removal of hydrogen or the loss of electrons (i.e. the gaining of a positive charge). Conversely, the term *reduction* is used to imply a gaining of electrons (i.e. a loss of positive charge). The loss of electrons as a common factor in oxidation processes is made more evident by considering such processes that occur in solution. The oxidation of ferrous ions to ferric ions may be depicted as follows—

$$Fe^{++} \rightarrow Fe^{+++} + e \quad . \quad . \quad . \quad . \quad (39)$$

whilst the oxidation of acetaldehyde to acetic acid by means of oxygen may be written as—

$$CH_3 . CHO + 2OH' \rightarrow CH_3 . COOH + H_2O + 2e \quad . \quad (40)$$

in both these reactions the symbol *e* representing one electron. In each case the oxidation process is accompanied by the liberation of electrons.

This result is quite usual so that it is possible to write the following general equation—

$$\text{Oxidized state} + \text{Electrons} \rightleftharpoons \text{Reduced state} \quad . \quad . \quad (41)$$

It follows therefore that an oxidizing agent may be regarded as a substance which reacts in such a manner as readily to take up electrons, becoming reduced itself in the process; whereas a reducing agent is a substance which is capable of readily yielding electrons, becoming oxidized in the process. These "oxidizing-reducing" reactions are often termed *redox* reactions. Thus a solution containing a mixture of ferrous and ferric ions will exhibit either oxidizing or reducing properties according as to whether it is capable of gaining or of losing electrons. This tendency may be determined by immersing in the solution a bright platinum electrode, as employed for measurements with the quinhydrone electrode. If the platinum electrode acquires a positive charge this indicates that electrons have been removed from the electrode; in other words the solution tends to oxidize the plate. On the other hand, if the solution is chemically reducing in nature, the platinum electrode will acquire a negative charge since the solution yields electrons to the electrode. Thus, on the platinum electrode there will be established a potential, the magnitude and sign of which will be determined by the oxidizing or the reducing power of the system.

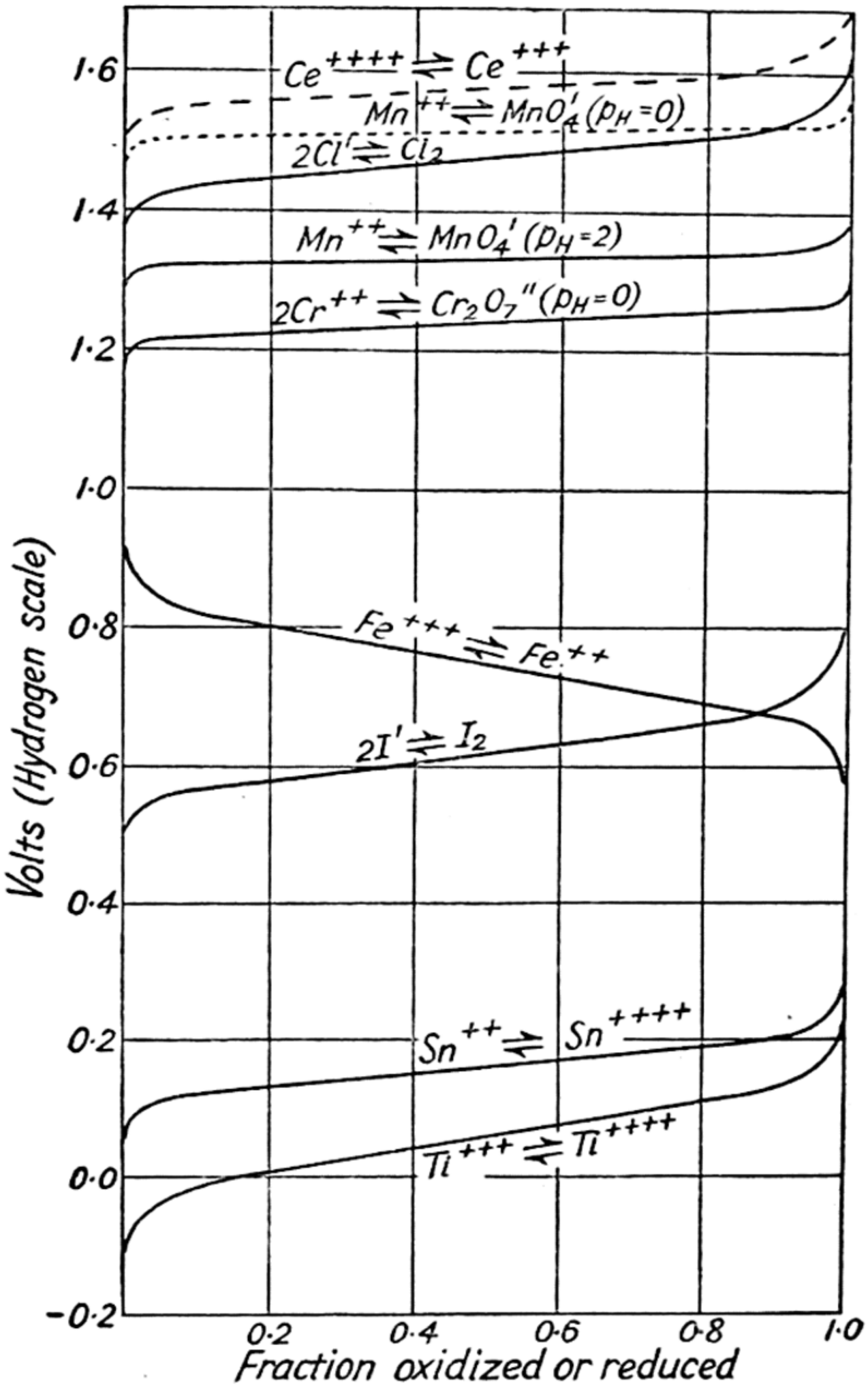


FIG. 113. Oxidation-Reduction Potentials

In order that an oxidizing or a reducing solution may impart a definite potential to an unattackable electrode such as platinum it is essential (*a*) that the oxidized and reduced forms must *both* be present in definite amounts, and (*b*) that both forms must be capable of conversion into the

other by an infinitesimally small change in the potential of the system in one direction or the other. Examples of such reversible systems are provided by ferric-ferrous, stannic-stannous, ferricyanide-ferrocyanide, and quinone-hydroquinone.

When a platinum electrode is immersed in any one of these or similar solutions it will acquire a definite potential E according to the *ratio* of the oxidized to the reduced form according to the expression—

$$E = E_0 + \frac{RT}{nF} \log_e \frac{[\text{concentration in oxidized state}]}{[\text{concentration in reduced state}]} \quad . \quad (42)$$

where E_0 = a constant, known as the standard oxidation-reduction potential of the system; R = gas constant; T = absolute temperature; n = the difference in the number of the electrons in the reduced and oxidized states respectively; and F = the faraday (96 500 coulombs).

Fig. 113 indicates the variation of potential when initially the solution consisted almost entirely of the reduced state of a given system and is gradually oxidized, as in the case of titration with an oxidizing agent. The *standard oxidation-reduction potential* of the system is that at which the solution is 50 per cent oxidized, and hence is given by the mid-point of each curve in Fig. 113. The standard oxidation-reduction potentials for a number of systems are quoted in Table 54.

TABLE 54

Standard Oxidation-Reduction Potentials at 25°C

System	Potential (volts)
Co^{++}, Co^{+++}	+ 1·82
Pb^{++}, Pb^{++++}	+ 1·75
Ce^{+++}, Ce^{++++}	+ 1·60
Mn^{++}, $MnO_4' + 8H^+$	+ 1·45
$\frac{1}{2}I_2$, $IO_3' + 6H^+$	+ 1·20
$\frac{1}{2}Hg_2^{++}$, Hg^{++}	+ 0·90
Fe^{++}, Fe^{+++}	+ 0·772
MnO_4'', MnO_4'	+ 0·664
$Fe(CN)_6''''$, $Fe(CN)_6'''$	+ 0·356
Cu^+, Cu^{++}	+ 0·16
Ti^{+++}, Ti^{++++}	+ 0·06
Sn^{++}, Sn^{++++}	− 0·15
Cr^{++}, Cr^{+++}	− 0·41

In general, any system higher in this table will oxidize another system lower down, and similarly any system will reduce one above it. The further apart are the standard oxidation-reduction potentials of two

systems, the more completely will that system with the more positive potential oxidize the other system. The trend of a curve depicting the change of potential on titration, towards the end point of an oxidation titration, depends however upon the nature of the titrant. If the standard oxidation-reduction potentials are reasonably well separated—that is, not less than approximately 0·3 volt—the oxidation reaction goes virtually to completion, but if the oxidation-reduction potentials of the two systems are close together neither system is able to oxidize or reduce the other to any appreciable extent.

Assuming that these oxidation-reduction potentials are well separated, the variations in the potential when an oxidant is added to a reductant

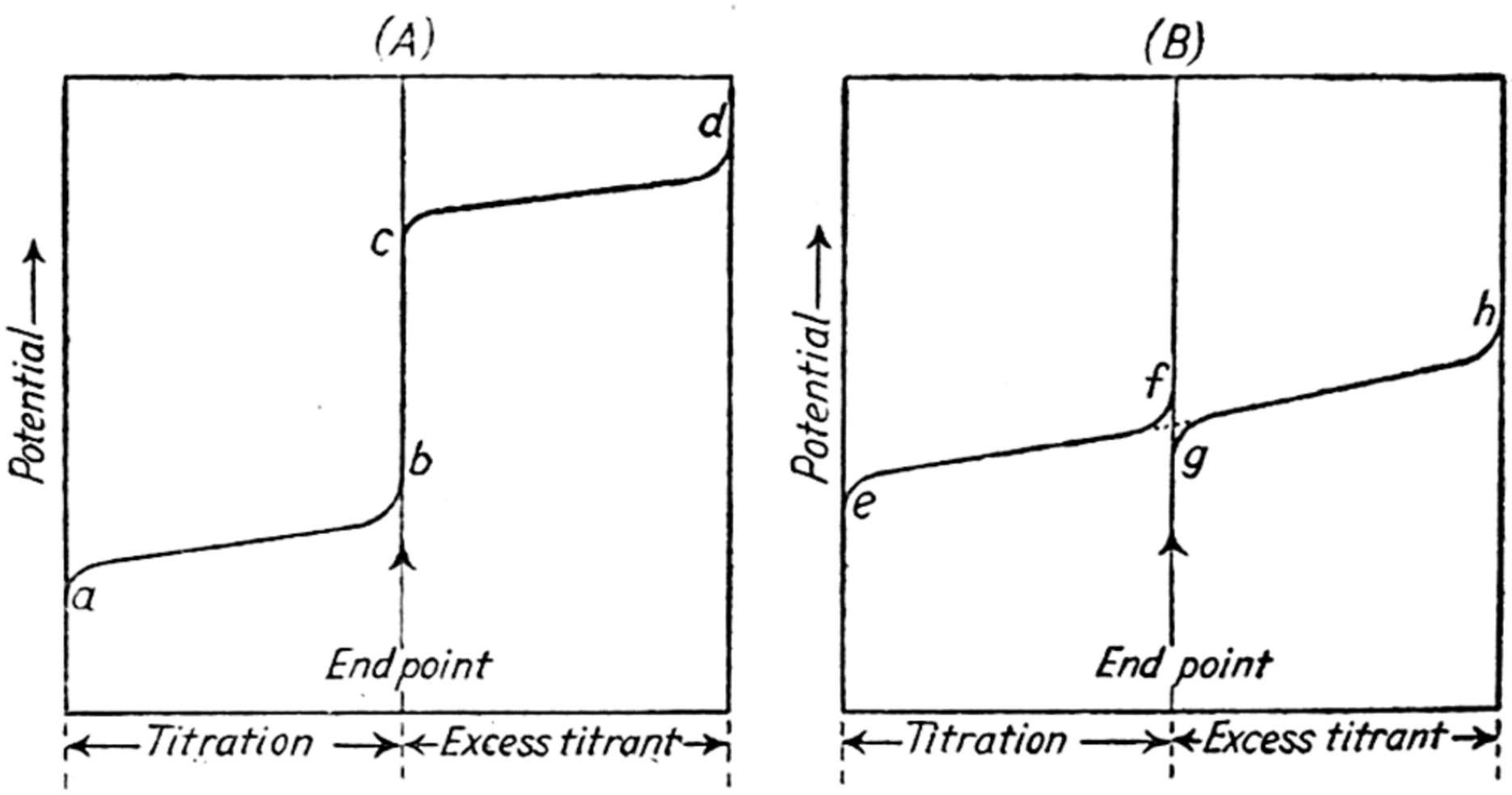


FIG. 114. Oxidation-Reduction Titration Curves

is such that during the oxidation the potential rises as shown by the curve *ab* (Fig. 114 (*A*)), and at the end point, when oxidation is complete, there is a sudden rise in the potential, portion *bc*, and the system assumes potential values characteristic of that system constituting the oxidizing medium. If the oxidation-reduction potentials of the two systems occur close together there is a gradual change of potential up to the titration end point which is more or less continued as the excess of titrant is added. This phenomenon is shown in Fig. 114 (*B*) where the curve *ef* represents the titration and the portion *gh* the addition of a progressively increasing excess of titrant. There are available a number of different substances which exhibit different colours in the oxidized and the reduced states and which are capable of adjusting themselves to the same potential of a system to which they are added; such substances are known as *oxidation-reduction indicators*. The potential of a system changes rapidly at the end point of a titration (for example, at point *b*, Fig. 114 (*A*)), and it follows that the colour of an oxidation-reduction indicator will also change at this same point, provided that it has been suitably chosen. In

other words, the standard potential for the indicator must lie between the standard oxidation-reduction potentials for the two systems being titrated if the colour change is to be a sharp one. Standard potentials for some oxidation-reduction indicators are given in Table 55. In addition, for satisfactory results to be obtained as regards a sharp end point the indicator standard potential should differ by at least 0·15 volt from the standard potential of the other systems involved.

TABLE 55

Oxidation-Reduction (Redox) Indicator Characteristics

Indicator	Colour Change on Oxidation	Standard e.m.f. (N . H_2 Electrode as Reference)	Preparation of Solution
		(volts)	
Methylene blue	Blue to colourless	0·53 ($p_H = 2·86$)	0·2 g in 100 ml of water
Diphenylamine	Colourless to violet	0·76	1 g in 100 ml conc. H_2SO_4 (0·006 M)
Diphenylbenzidine	Colourless to violet	0·76	1 g in 100 ml conc. H_2SO_4 (0·003 M)
Ba-diphenylamine sulphonate (Na_2SO_4 used to ppt. Ba as $BaSO_4$)	Colourless to reddish-violet	0·84	3·17 g/litre of water (0·005 M)
Eriogreen	Reddish-yellow to rose	0·99	0·1 g/100 ml water
Erioglaucine	Reddish-yellow to rose	1·00	0·1 g/100 ml water
Methyl ferroin (5-methyl-1, 10-phenanthroline ferrous sulphate)	Red to pale blue	1·02	
p-nitro-diphenylamine	Colourless to violet	1·06	1 g in 100 ml conc. H_2SO_4
Ferroin (1, 10-phenanthroline ferrous sulphate)	Red to pale blue	1·06	
N Phenanthranilic acid	Colourless to pink	1·08	1·07 g in 20 ml of 5 per cent Na_2CO_3 and dilute to 100 ml (0·005 M)
Nitro ferroin (5-nitro-1, 10-phenanthroline ferrous sulphate)	Red to pale blue	1·25	
Ruthenium tripyridyl nitrate	Yellow to colourless	1·25	

Decomposition Voltage. If a gradually increasing d.c. potential is applied to two electrodes composed of bright platinum foil *A* and *C* (Fig. 115), which are immersed in an electrolyte *E* composed of a dilute aqueous solution of sulphuric acid, the relationship of the applied potential to the current flowing through the electrolyte is as shown graphically in Fig. 116. This process of electrolysis gives rise to the liberation of oxygen and hydrogen at anode and cathode respectively, establishing what are in effect two gas electrodes which are capable of exerting a back e.m.f. in opposition to that exerted by the battery *B*. The existence of this back e.m.f. may be demonstrated by opening the switch *S*, after previously

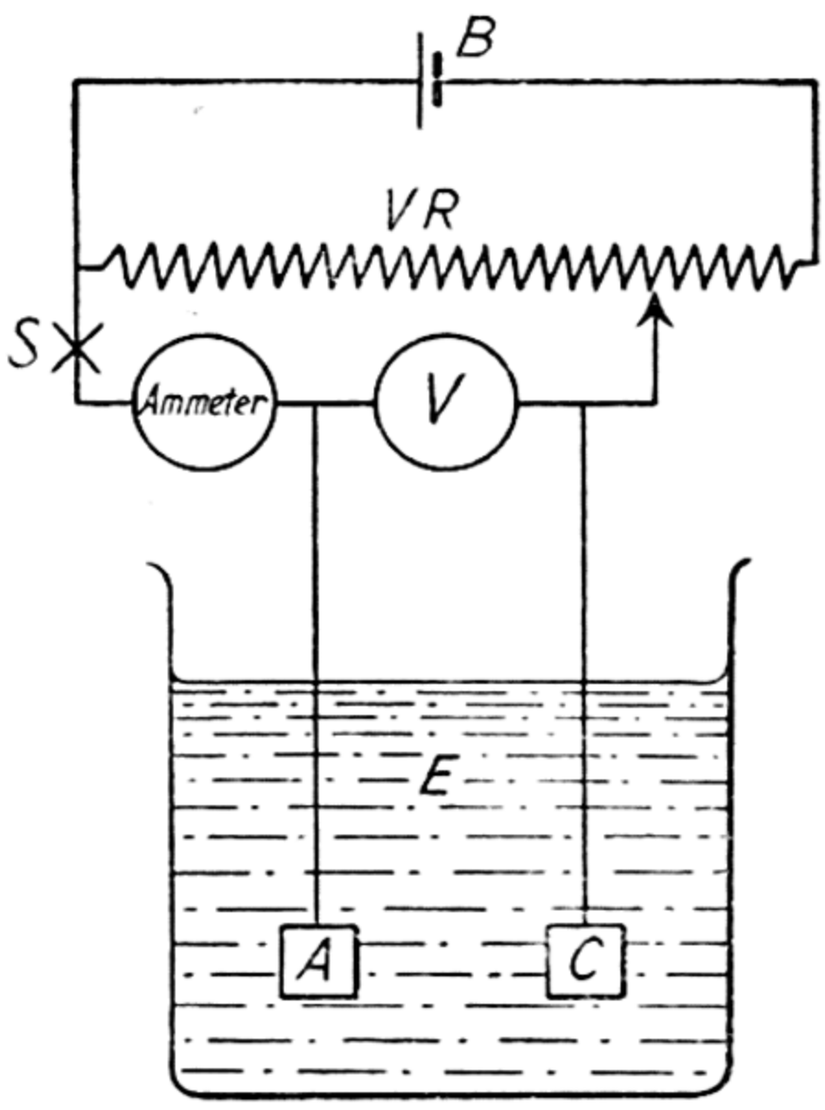


FIG. 115. Determination of Decomposition Voltage

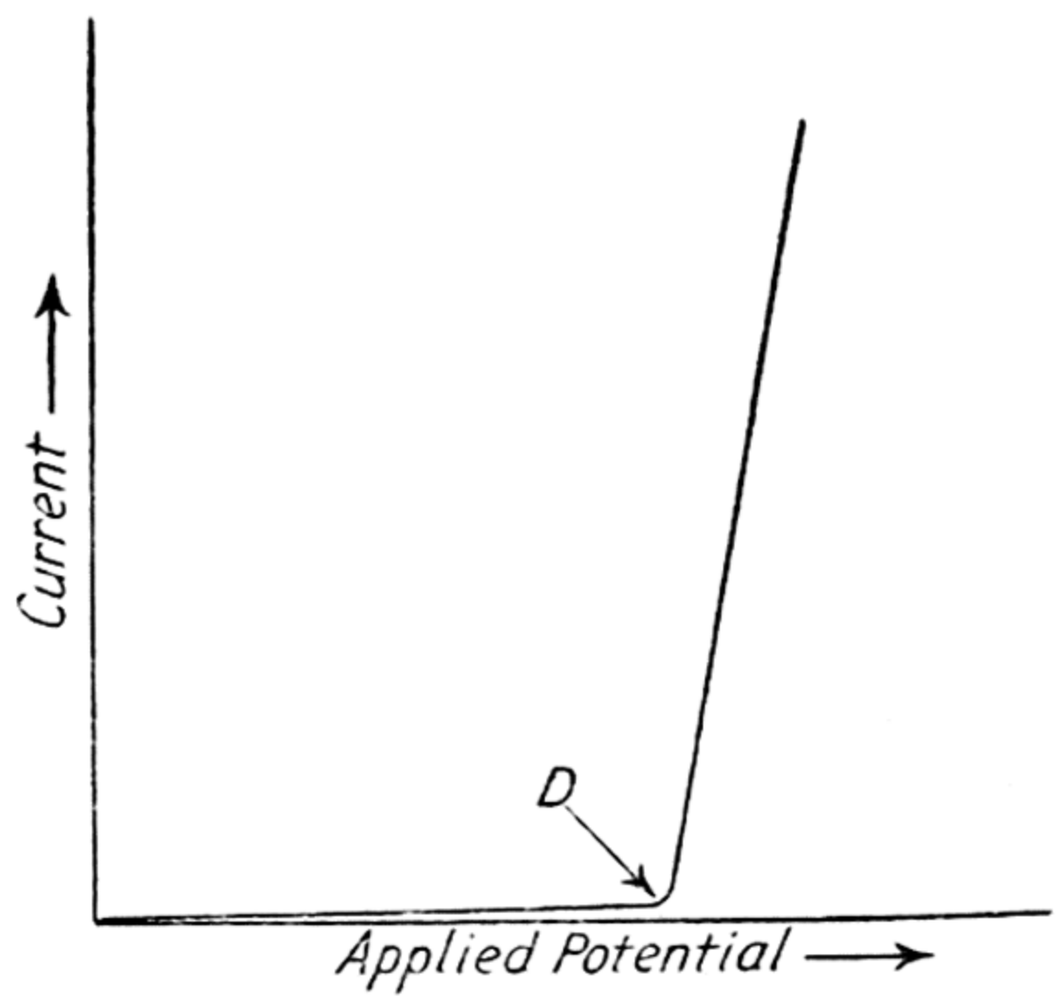


FIG. 116. Current—Applied Potential Curve

allowing the electrolysis to proceed for a few minutes, when the voltmeter *V* will indicate the voltage set up by the oxygen-hydrogen cell.

At low values of applied potential the very slow rates of diffusion of liberated oxygen and hydrogen permit the almost perfect shrouding of the electrodes with these gases, and the back e.m.f. which these two gas electrodes set up is practically equal to the applied potential. As the applied potential is increased the back e.m.f. also increases until a maximum value is reached for the latter; this is represented by the point *D* (Fig. 116). This point at which steady electrolysis occurs is known as the *decomposition voltage*.

Polarization of Electrodes. When current is passed into a cell, such as the oxygen-hydrogen gas cell described above, so as to raise the potential of the cell terminals above their static value—that is above the decomposition voltage—the cell is said to be *polarized*, and the phenomenon exhibited is known as *electrolytic polarization* or simply *polarization*.

In a similar manner, when the potential of a primary cell falls below its static e.m.f. value, such a cell is also said to be polarized. It will thus be clear that an electrode has a characteristic, reversible potential representing its condition of equilibrium; if its potential is raised above this figure the electrode is said to be *anodically polarized*, whilst it is *cathodically polarized* when its potential is lowered below the equilibrium value. When an electrode is anodically polarized current will flow in one direction; when it is cathodically polarized current will flow in the opposite direction.

In the case of the electrolysis of aqueous solutions of metallic salts there are produced differences in the concentration of the electrolyte at the electrode surfaces; this phenomenon is known as *concentration polarization*. It can be minimized by stirring the electrolyte, by increasing the salt concentration, or by raising the temperature, but it cannot be entirely eliminated. Thus, for example, if an aqueous solution of cupric sulphate is electrolyzed between copper electrodes, the copper anode dissolves giving rise to an increase in the cupric ion concentration in its vicinity, whilst the deposition of copper on the cathode results in an impoverishment of cupric ions in the vicinity of the cathode. There is established therefore, a concentration cell which produces a back e.m.f. in opposition to the applied e.m.f., giving rise to a definite tendency for the concentrations of the anolyte and catholyte to be equalized by deposition of copper on the anode, and dissolution of copper from the cathode.

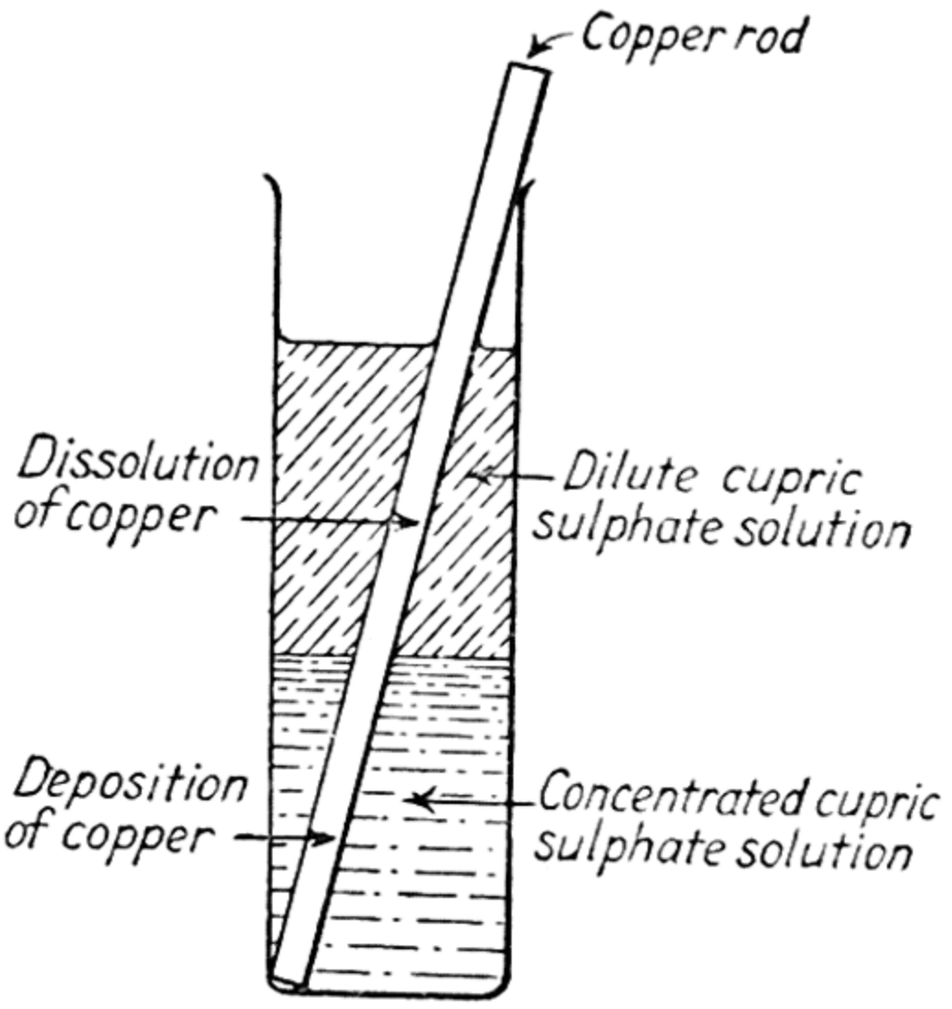


FIG. 117. Concentration Polarization

In general, the magnitude of concentration polarization is small since it will be recalled that according to the Nernst equation (32*a*) a ten-fold change of ionic concentration will only result in a change of 0·058 volt or 0·029 volt for univalent and bivalent ions respectively.

The existence of the effects described above may be readily illustrated by a simple experiment in which a copper rod is placed vertically in a cell containing a lower layer of a concentrated aqueous solution of cupric sulphate and a weaker solution of the same salt above it (*see* Fig. 117.) If after a time the copper rod is removed it will be noted that a copper deposit has been laid down from the lower, stronger solution, whilst copper has been dissolved anodically from that portion of the rod immersed in the upper, weaker solution. Similarly, the Daniell cell may exhibit concentration polarization since on yielding current the zinc

electrode dissolves, thereby increasing the concentration of zinc ions in its vicinity and making the potential of this electrode less negative; whilst at the copper electrode, copper is "plated" out and the concentration of cupric ions in its vicinity reduced thereby rendering this electrode less positive. In this specific case, concentration polarization may be minimized by employing saturated aqueous solutions of cupric sulphate and zinc sulphate containing crystals of these salts; thus, concentration changes

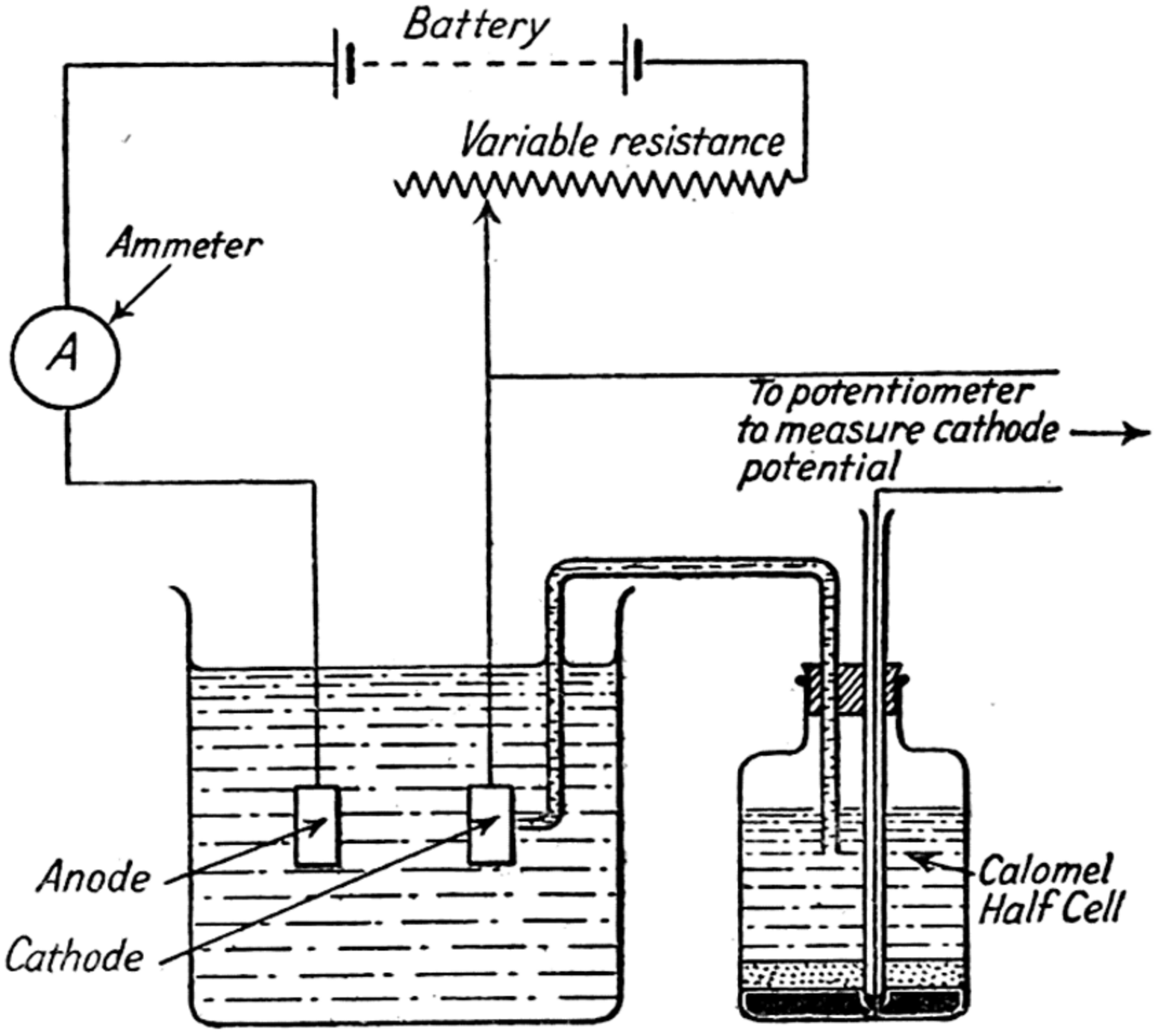


FIG. 118. Circuit Arrangement for Studying Electrolysis with Constant Current

are reduced to a minimum and the cell e.m.f. remains practically constant when supplying current.

Depolarization. If an oxidizing agent is added to an electrolytic cell in which polarization has occurred due to the accumulation of hydrogen, the hydrogen can be removed as fast as it is liberated and the potential of the electrode is thereby unaffected. Such an added substance which acts in this manner is known as a *depolarizer*, or more specifically in this particular type of example, a *cathodic depolarizer*. Polarization at an anode may be reduced by the addition of a suitable reducing agent which is thus termed an *anodic depolarizer*.

In primary cells various depolarizers are employed; in the Leclanché cell, manganese dioxide is used, while in the Poggendorf (dichromate) cell use is made of an acid solution of potassium dichromate. Similarly, in the calomel half-cell, the solid mercurous chloride acts as a depolarizer since it prevents any appreciable alteration in the concentration of

mercurous ions in the vicinity of the mercury electrode such as may result from the accidental withdrawal from, or passage through the cell of excessive current during e.m.f measurements. Similarly, cupric sulphate and zinc sulphate in the Daniell cell may be regarded as depolarizers since they prevent disturbance of the electrode equilibria.

Discharge Potentials at Separate Electrodes. Using the apparatus shown in Fig. 115 it is possible to determine the decomposition voltages of electrolytes other than dilute sulphuric acid. Some typical results are given in Table 56.

TABLE 56

Decomposition Voltages of Normal Aqueous Solutions using Bright Platinum Electrodes

Solution	Decomposition Voltage	Solution	Decomposition Voltage
Sulphuric acid	1·67	Zinc sulphate	2·35
Nitric acid	1·69	Zinc bromide	1·80
Phosphoric acid	1·70	Nickel sulphate	2·09
Dichloracetic acid	1·66	Nickel chloride	1·85
Malonic acid	1·69	Lead nitrate	1·52
Perchloric acid	1·65	Cadmium nitrate	1·98
Tartaric acid	1·62	Cadmium sulphate	2·03
Sodium hydroxide	1·69	Cadmium chloride	1·88
Potassium hydroxide	1·67	Cobalt chloride	1·78
Ammonium hydroxide	1·74	Cobalt sulphate	1·92
Methylammonium hydroxide (N/4)	1·75	Silver sulphate	0·80
Diethylammonium hydroxide (N/2)	1·68	Silver nitrate	0·70
Tetramethyl-ammonium hydroxide (N/8)	1·74		
Hydrochloric acid	1·31		
Hydrobromic acid	0·94		
Hydriodic acid	0·52		

From the above table it will be noted that all the acids and bases, except the halogen acids, have decomposition voltages in the region of 1·7 volts from which it is argued that although the current is carried by different kinds of ions in the different electrolytes, these ions are not necessarily those which are discharged; in actual fact the process common to the electrolysis of all such aqueous solutions is the cathodic discharge of hydrogen ions and the anodic discharge of hydroxyl ions.

In order to determine whether or not any particular ion may be discharged it is necessary to measure the separate potential at each electrode during the actual process of electrolysis. This may be done by using the circuit arrangement shown in Fig. 118. The variation with current of cathode potential for some common metals in aqueous solutions of their salts is shown in Fig. 119. The similarity of these curves to that shown in Fig. 116 should be noted, the point *D* (Fig. 116) now corresponding to the

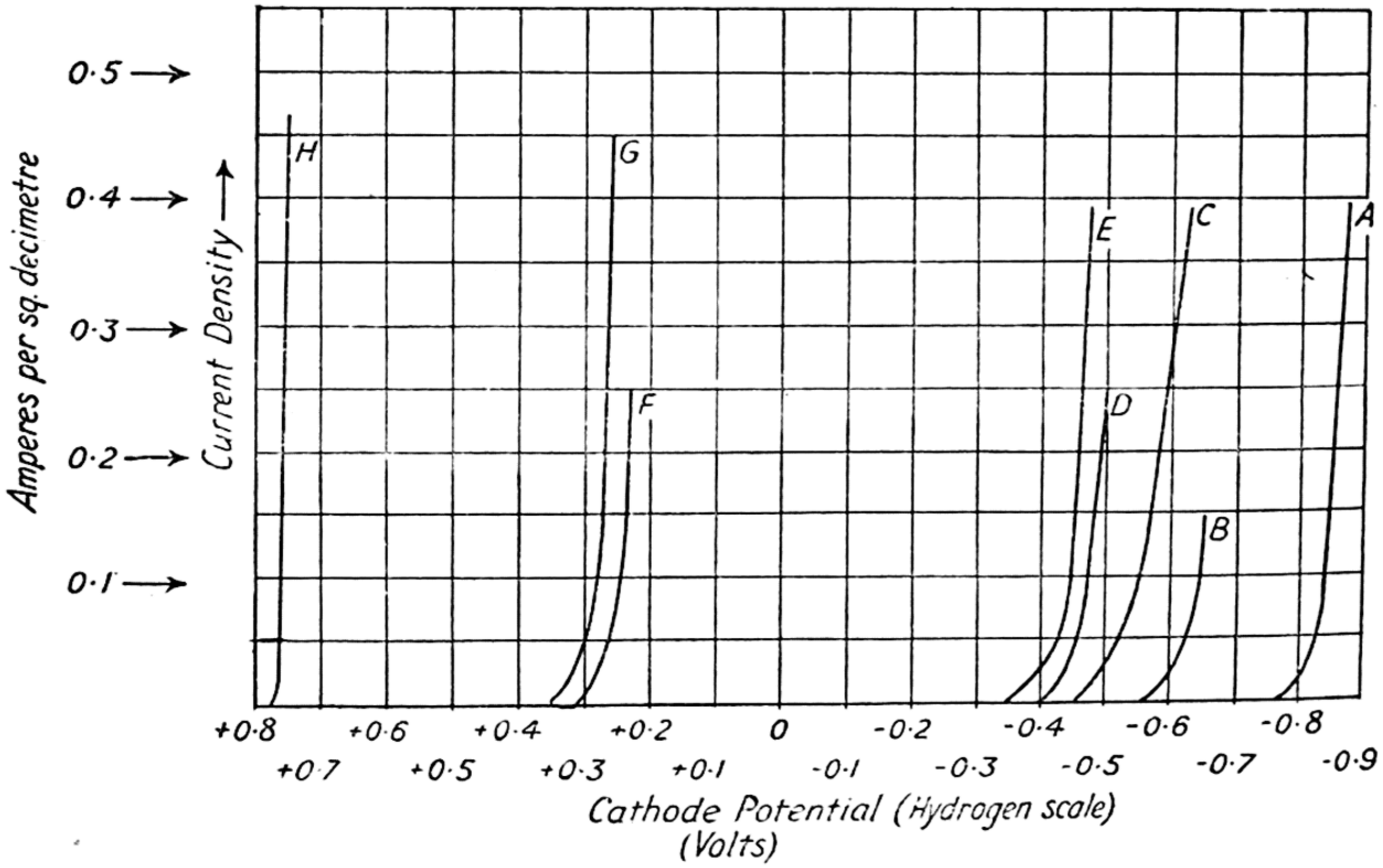


FIG. 119. Variation with Current of Cathode Potential for some Common Metals

A = Copper in N.copper sulphate solution
B = Copper in N/10 copper sulphate solution
C = Cobalt in N.cobalt sulphate solution
D = Cadmium in N.cadmium sulphate solution
E = Nickel in N.nickel chloride solution
F = Iron in N.ferrous sulphate solution
G = Zinc in N.zinc sulphate solution

so-called *deposition potential* (or *discharge potential*) at the particular metal electrode. With increasing current the cathode potential becomes slightly more negative probably as a result of concentration polarization.

It has been found that in general the deposition potential of a metal is equal to the static or equilibrium potential which the deposited metal exhibits in the same solution. The decomposition voltage of an electrolyte is equal to the algebraic difference of the potentials of the two separate electrodes, and at the decomposition point both electrodes have attained their decomposition potentials and ions may discharge freely at both anode and cathode.

The disposition with respect to one another of the curves shown in Fig. 119 is of very considerable importance in connexion with the deposition of metals both in respect of the technological aspects of metals and alloy deposition in practical electroplating, and also in respect of the analytical separation of metals by electrodeposition. If a steadily increasing e.m.f. is applied to an electrolytic cell, the single potential of the cathode becomes increasingly more and more negative, whilst the anode becomes increasingly positive, so that if a number of processes are possible at an electrode surface they will occur in order as the electrode potential attains the value corresponding to each such process. Thus, in an electrolysis using bright platinum electrodes in an acid solution of copper sulphate, the deposition potential of cupric ions is approximately + 0·34 volt—namely, the same as the static equilibrium potential—whilst the deposition potential of hydrogen ions is approximately − 0·1 volt; therefore the deposition of copper on the cathode will occur in preference to the liberation of hydrogen at the same electrode since the former has the least negative potential. When the copper has been almost completely deposited from solution then on increasing the applied e.m.f., so that the cathode becomes more negative, the evolution of hydrogen occurs.

As the concentration of the ions of the deposited metal decreases during the electrolysis, its deposition potential becomes progressively more negative and may even in fact approach that for the deposition of another metal. Thus, from equation (32*a*) it follows that the electrode potential of a metal is diminished by $0{\cdot}058/n$ volt (where n = valency) for each ten-fold reduction of the metal ion concentration. This general tendency is exemplified by curves, *B* and *A* (Fig. 119), the former depicting the cathode potential of copper in 0·1N cupric sulphate solution, and the latter the cathode potential of copper in a normal solution of the same salt. If at the commencement of electrolysis the concentration of the metal ion is C, then with a bivalent metal like copper the cathode potential E_1 will be—

$$E_1 = E_0 + \frac{0{\cdot}058}{n} \log_{10} C_1 \quad . \quad . \quad . \quad (32a)$$

and since $n = 2$ in this case—

$$E_1 = E_0 + 0{\cdot}029 \log_{10} C_1 \quad . \quad . \quad . \quad . \quad (43)$$

If deposition is allowed to continue until the metal ion concentration is one tenth of its initial value, then the new cathode potential, E_1' will be—

$$\begin{aligned} E_1' &= \mathrm{E}_0 + 0{\cdot}029 \log_{10} (C_1 \times 10^{-1}) \\ &= E_0 + 0{\cdot}029 \log_{10} C_1 + 0{\cdot}029 \log_{10} 10^{-1} \\ &= (E_0 + 0{\cdot}029 \log_{10} C_1) - 0{\cdot}029 \\ &= \text{potential at commencement of deposition} - 0{\cdot}029 \text{ volt}. \quad . \quad (44) \end{aligned}$$

The changes in cathode potential taking place during electrolysis of solutions from which discharge either univalent or bivalent ions are given in Table 57.

TABLE 57

Changes in Cathode Potential

Concentration of Metal Ions	Cathode Potential (volts)	
	Univalent Ions Being Discharged	Bivalent Ions Being Discharged
Initial concentration (C)	E_1	E_1
$C \times 0{\cdot}1$	$E_1 - 0{\cdot}058$	$E_1 - 0{\cdot}029$
$C \times 0{\cdot}01$	$E_1 - 0{\cdot}116$	$E_1 - 0{\cdot}058$
$C \times 0{\cdot}001$	$E_1 - 0{\cdot}174$	$E_1 - 0{\cdot}087$
$C \times 10^{-4}$	$E_1 - 0{\cdot}232$	$E_1 - 0{\cdot}116$
$C \times 10^{-5}$	$E_1 - 0{\cdot}290$	$E_1 - 0{\cdot}145$
$C \times 10^{-6}$	$E_1 - 0{\cdot}348$	$E_1 - 0{\cdot}174$

Since in electrolytic analysis it is desirable that the metal ion concentration at the end of the determination should be below 0·0001 of the initial concentration, it is necessary that the final voltage drop at the cathode should be 0·232 volt in the case of a univalent metal and 0·116 volt for a bivalent metal. In other words, an excess voltage of 0·25 volt would reduce the metal ion concentration to such a low value as to be undetectable by the ordinary methods of chemical analysis.

It also follows that in a mixed solution of two metal salts, the analytical separation of one metal from the other may be effected if the initial deposition potentials of the two metals differ by not less than 0·25 volt. Thus, in the case of a solution containing molar quantities of cadmium and zinc salts, on electrolysis cadmium commences to be deposited when the cathode potential is approximately — 0·4 volt, whilst zinc does not begin to be deposited until the cathode potential is approximately — 0·76 volt. Since these two metals have initial deposition potentials differing by 0·36 volt an effective analytical separation of one metal from the other is readily possible.

Overvoltage. Although at a platinized platinum electrode hydrogen is liberated from dilute sulphuric acid practically at the reversible hydrogen potential for that solution, when electrodes of other metals are employed a more negative potential is required to bring about hydrogen liberation. The voltage difference between the reversible hydrogen potential and that at which visible gas evolution occurs at a metal electrode in the same solution is known as the *hydrogen overvoltage* of the metal concerned. Some typical values for hydrogen overvoltage are given in Table 58.

TABLE 58

Hydrogen Overvoltages in Dilute Sulphuric Acid

Metal Constituting Cathode	Hydrogen Overvoltage (volts)
Platinized platinum	0·005
Gold	0·02
Iron (in NaOH)	0·08
Smooth platinum	0·09
Silver	0·15
Nickel	0·21
Copper	0·23
Cadmium	0·48
Tin	0·53
Lead	0·64
Zinc	0·70
Mercury	0·78

Taking a specific example, these results mean that whereas gaseous hydrogen is evolved from a mercury cathode in dilute sulphuric acid when the cathode potential has a value on the hydrogen scale of — 0·78 volts, at a nickel cathode in the same electrolyte, hydrogen will be evolved when this electrode's potential is only — 0·21 volt. The overvoltage decreases as the surface of the cathode becomes more rough, and increases as the current density increases.

Overvoltage effects are also noted in the liberation of oxygen at the anode. Values for oxygen overvoltages for a number of metals are given in Table 59.

TABLE 59

Oxygen Overvoltages in Dilute Sulphuric Acid

Metal Constituting Anode	Oxygen Overvoltage (volts)
Nickel (spongy)	0·05
Nickel	0·12
Cobalt	0·13
Iron	0·24
Platinized platinum	0·24
Lead	0·31
Silver	0·41
Smooth platinum	0·44
Gold	0·53

Now the theoretical value for the e.m.f. of the hydrogen-oxygen cell as calculated from free energy data is 1·22 volts, and using bright platinum electrodes for the electrolysis of dilute sulphuric acid, the hydrogen and oxygen overvoltages are 0·09 volts and 0·44 volt respectively. Thus, the decomposition voltage of this acid, and indeed all acids (and alkalis) yielding gaseous oxygen and hydrogen at anode and cathode respectively, should be equal to the sum of the theoretical gas cell e.m.f. and the two overvoltages; that is $1{\cdot}22 + 0{\cdot}09 + 0{\cdot}44 = 1{\cdot}75$ volts. Reference to Table 56 shows that in general such is the case.

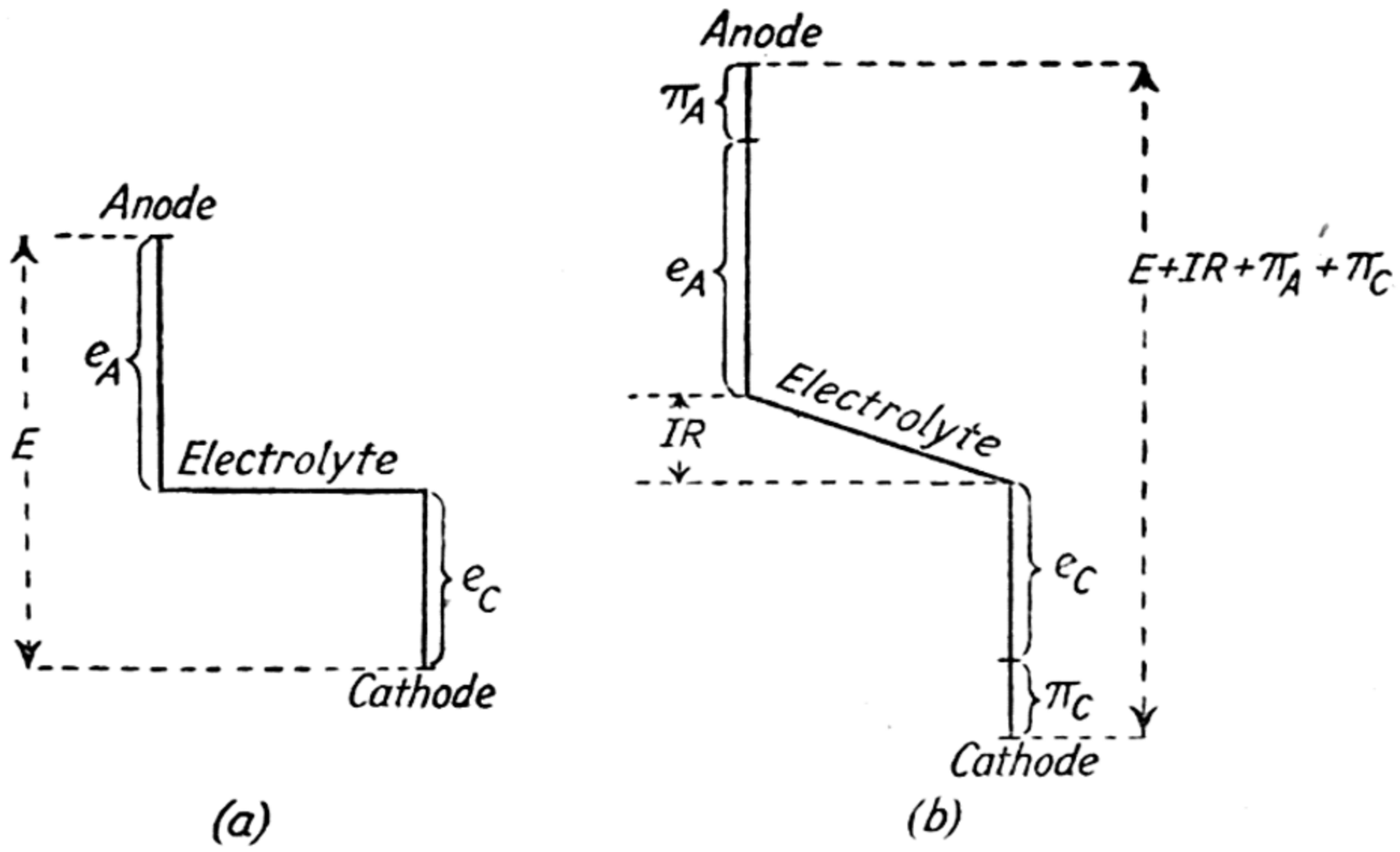


FIG. 120. Variation of Potential through a Simple Electrolytic Cell (*a*) when the Electrode Equilibria are Established, but no Current is Passing, and (*b*) when Current is Passing and Electrolysis is therefore Taking Place

Thus, in order that any particular electrolysis may proceed at a given rate the applied voltage must exceed the reversible decomposition voltage E by an amount dependent on the following factors—

(i) The cathode polarization, π_c volt, at the current density employed.

(ii) The anodic polarization, π_a volt, at the current density employed.

(iii) The electrical resistance, R ohm, of the current path from anode to cathode through the electrolyte; this resistance includes that of a diaphragm where such is employed to separate the anolyte from the catholyte. If the current is I amp., then the voltage drop through the electrolyte will be IR volt.

Thus, the voltage V which must be applied to an electrolytic cell to cause electrolysis to proceed at a given rate is represented by the following expression—

$$V = E + IR + \pi_c + \pi_a \text{ volts}$$

Fig. 120 depicts diagrammatically the variation of potential through a simple electrolytic cell, (*a*) when the electrode equilibria are established, but no current is passing, and (*b*) when current is passing and electrolysis is therefore taking place. In this diagram, e_A and e_C represent the electrode potentials of the anode and cathode respectively.

Simultaneous Electrodeposition of Metals. If the deposition potentials of two metals are such that one of the metals is appreciably less negative than the other, the current-density/cathode-potential curves will be as shown in Fig. 121. At all reasonable values of current density the deposit will consist solely of metal *A*, since the deposition potential in metal *B* is not attained. Such is the case with the two metals copper and zinc which may be deposited separately from aqueous solutions of their mixed sulphates since the deposition potentials of copper and zinc are + 0·34 volt

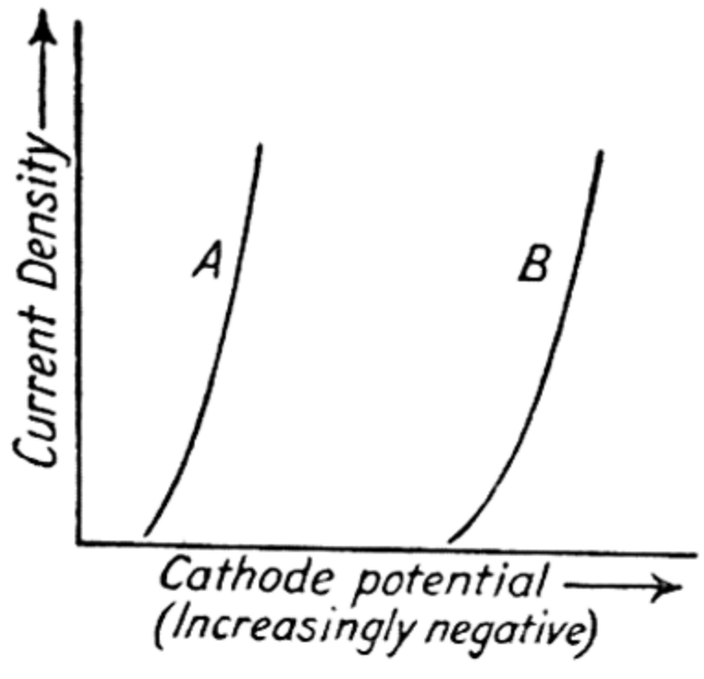


FIG. 121. Cathode Potentials for Two Metals when Alloy Deposition is Impossible

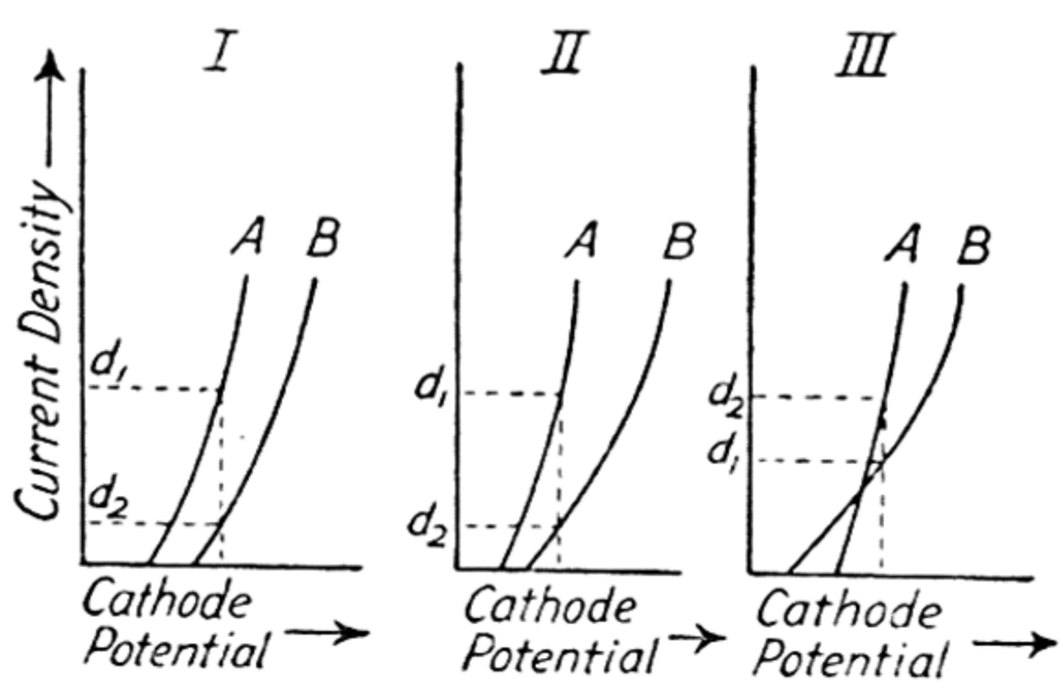


FIG. 122. Cathode Potentials for Two Metals when Alloy Deposition is Possible

and — 0·76 volt respectively. This condition is desired in analysis for the quantitative separation of two metals by electrodeposition.

It should be noted, however, that the deposition potentials may be varied by changing the electrolyte so that under the changed conditions analytical separation may not be possible. For example, if an excess of an alkali cyanide is added to the mixed aqueous solution of copper and zinc sulphates, both these metals form complex cyanides from which solution *both copper and zinc are simultaneously electrodeposited* as an alloy, when the cathode potential is approximately — 1·0 volt. This simultaneous electrodeposition of two or more metals whose deposition potentials are nearly equal, i.e. *alloy deposition*, is of considerable technological importance. In alloy deposition the current-density/cathode-potential curves lie close together, but in respect of their mutual disposition three possibilities are open; namely, (*a*) the two curves for the two metals *A* and *B* may be more or less parallel to one another as depicted in Fig. 122 at *I*; (*b*) with increasing current density the two curves may diverge as shown in Fig. 122 at *II*; and finally, there is the possibility that

the two curves may converge, intersect and then diverge as shown in Fig. 122 at *III*.

If it is assumed that metal *A* is more noble than metal *B*, then only *A* will be deposited until a current density is attained at which the cathode potential corresponds to the deposition potential of metal *B*; when this condition exists metals *A* and *B* will be deposited simultaneously. Further increase in current density causes the co-deposition of both metals in proportions dependent upon the disposition of the curves. In general, however, metal *A* deposits at a rate proportional to the current density d_1 (Fig. 122), and metal *B* to d_2 where d_1 and d_2 are the current densities at which metals *A* and *B* both have the same cathode potential. Thus, when both metals have the same cathode potential the fraction $d_1/(d_1 + d_2)$ of the total current will be used in depositing metal *A*, and the fraction $d_2/(d_1 + d_2)$ in depositing metal *B*, and the deposit will consist of metals *A* and *B* in the ratio of d_1 to d_2 equivalents.

In the case depicted in Fig. 122 at *I*, $(d_1 - d_2)$ is almost constant and the ratio d_1/d_2 decreases with increasing current density; the proportion of metal *A* in the deposit therefore decreases as the current density increases. In Fig. 122 at *II* the ratio d_1/d_2 remains almost constant with increasing current density and thus the composition of the deposit will also remain constant. In Fig. 122 at *III* the deposit will consist of equivalent amounts of the two metals when the current density corresponds to the point of intersection of the two curves; below this particular current density, however the deposit will consist of an excess of metal *A*, whilst at current densities in excess of that of the point of intersection the deposit will contain an excess of metal *B*. In actual practice there is always some metal ion impoverishment in the catholyte and this favours the deposition of the less noble metal.

Simultaneous Electrodeposition of Metal and Hydrogen. Although in the discussion just concluded the only ions suffering discharge were taken to be metal ions, the electrolysis of aqueous solutions very often involves the cathodic discharge of hydrogen ions. If at all current densities the deposition potential of a metal is more positive than that of hydrogen, only the metal will be deposited; in this case, curve *B* (Fig. 121) may be regarded as representing the current-density/cathode-potential curve for hydrogen. Such is the case when aqueous solutions of copper sulphate are electrolyzed. If, however, an excess of an alkali cyanide is added to this solution the deposition potential of copper is changed to a much more negative value, more negative in fact than that of hydrogen; in other words, curve *A* (Fig. 121) now represents the current-density/cathode-potential curve for hydrogen, whilst curve *B* represents that for copper; from such a solution, hydrogen is discharged preferentially. This condition also applies to metals which decompose water and in such cases even the reduction of hydrogen ion concentration by the employment of neutral

solutions is of no avail in assisting the preferential deposition of the metal.

Metal and hydrogen are capable of simultaneous deposition when their current-density/cathode-potential curves are related to one another as shown in one or other of the three variants depicted in Fig. 122. In such cases the efficiency of metal deposition will be affected by variation of current density in the manner as described above under the discussion of the simultaneous electrodeposition of metals.

ELECTROPLATING

Electroplating is the commercial production by electrodeposition of coatings of metals or of alloys on metallic objects, and to some extent on non-metallic objects (e.g. plastics and ceramics). Such electrodeposited coatings are usually very thin (e.g. 0·00001 — 0·001 in.), although for certain engineering purposes thicker coatings (e.g. 0·0625 — 0·125 in.) are employed.

Electrodeposited coatings are often laid down with the object of enhancing the corrosion resistance of the underlying base metal; in this way articles may be fabricated from low cost materials (e.g. steel) which are subsequently electroplated to lengthen their useful working life. The thinner electrodeposited coatings are also often employed to enhance the decorative appearance of the plated article. The process of electrodeposition thus assumes considerable economic importance in industry.

Thick electrodeposits are applied to engineering components either (*a*) for the purpose of laying down on the body of the article (e.g. engineering inspection gauges) a hard, and therefore wear-resistant, coating; for this purpose chromium is widely employed; or alternatively, (*b*) with the object of building up to correct dimensions, engineering components which have become partly worn away in service (e.g. hydraulic ram shafts), or components which have become overmachined during fabrication and which if not built up by electrodeposition would have to be scrapped; for such building up purposes nickel is widely employed as the electrodeposited metal.

In technical electroplating the article to be coated constitutes the cathode in an electrolyte containing ions of the metal to be plated out. The anode is often the same metal as that undergoing deposition on the cathode, such anodes being termed *soluble anodes*. In certain electroplating processes (e.g. chromium plating) *insoluble anodes* are employed, the metal plated out being derived entirely from the metallic salt dissolved in the plating bath.

With the object of obtaining firmly adherent and impervious electrodeposited coatings it is necessary that, previous to electroplating, the base

metal should be freed from foreign matter. Such foreign matter may be of two kinds—

(1) *Rust, scale and tarnish coatings and similar matter.* These are removed by processes of mechanical abrasion and by pickling in acids; generally sulphuric acid is employed although hydrochloric acid and other acid solutions are sometimes used. The process of electrolytic pickling is also employed in which the object to be treated is made the cathode in an electrolyte usually consisting chiefly of sulphuric acid, the anodes being of lead. The temperature of the electrolyte may be varied from room temperature to nearly boiling point.

(2) *Grease, oil, lacquer, paint and dirt.* These are removed by immersion of the work in alkaline cleaners which often contain oxide-solvent substances such as cyanides, and detergents such as trisodium phosphate. Sometimes the work undergoing cleaning is either made the cathode in such solutions, or alternatively made anode and cathode alternately. In such electrolytic baths cleaning takes place partly as a result of the formation of free alkali at the cathode, and partly due to the cathodic liberation of hydrogen which helps to remove mechanically the films of grease, oil, etc., and to assist in their emulsification. In many plating plants grease is often removed by immersion of the work in the vapour of organic solvents (e.g. trichlorethylene).

After cleaning, the work is subjected to mechanical polishing, and in certain cases to further pickling by immersion in a solution known as a *bright dip* consisting of a mixture of concentrated sulphuric and nitric acids.

The plating bath itself may be regarded as being made up of one or more of a number of different components—

(*a*) The salt or the acid from which the metal is deposited.

(*b*) Buffer additions should it be necessary to operate the bath over a narrow p_H range.

(*c*) Addition agents to prevent "anode passivity," that is, to increase the rate of solution of the anode if the salt or the acid detailed as component (*a*) is insufficiently corrosive in respect of anode attack.

(*d*) An additional salt to enhance the electrolytic conductivity of the plating bath, should this not be of a sufficiently high value by the presence of component (*a*).

(*e*) Addition agents to affect the crystalline nature of the electrodeposit.

Plating baths differ considerably in that some contain all the above mentioned components, whilst in others, one substance is capable of acting in more than one capacity. For example in the Watts type nickel plating bath, nickel sulphate provides the metal ion, boric acid serves as a buffer to maintain the p_H of the solution within close limits, ammonium chloride increases the conductivity of the bath, and nickel chloride assists solution of the anode. Metals are electrodeposited within specific

ranges of current density and temperature outside which unsatisfactory deposits are obtained.

TABLE 60

Chief Characteristics of Typical Plating Baths

Metal or Alloy	Bath Type	Anode	Current Density (Amps/ft²)	Temperature (°C)
Cadmium	Alkaline cyanide	Cadmium	10–30	20–30
Chromium	Chromic acid	Antimonial lead	100–200	45–60
Cobalt	Single sulphate	Cobalt	30–150	Up to 35
Copper	(*a*) Acid sulphate	Copper	25–30	Room temp.
	(*b*) Alkaline cyanide	Copper	10–20	35–40
	(*c*) Rochelle salt	Copper	20–60	60–70
Gold	Cyanide	Gold, carbon, stainless steel or platinum	1–5	60–80
Iron	(*a*) Chloride	Iron	100–180	90–110
	(*b*) Double sulphate	Iron	20–30	20–30
Lead	Fluoborate	Lead	10–30	20–30
Nickel	Single sulphate	Nickel	20–40	20–35
Platinum	Phosphate	Carbon or platinum	1	70
Rhodium	(*a*) Acid sulphate	Platinum	10–100	40–45
	(*b*) Acid phosphate	Platinum	10–40	30–40
Silver	Cyanide	Silver (999 fine)	5–10	15–25
Tin	(*a*) Chloride	Tin	10	50
	(*b*) Alkaline stannate	Tin	10–20	70–80
	(*c*) Acid bath	Tin	5–10	20–30
Zinc	(*a*) Sulphate	Zinc	10–30	20–30
	(*b*) Chloride	Zinc	15–150	20–40
	(*c*) Alkaline cyanide	Zinc	8–20	40–50
Brass	Cyanide	Brass (67–80 per cent Cu)	10–30	40–60
Bronze	Cyanide	Separate tin and copper	25	65

The electrodeposited coating after withdrawal from the plating bath is often dull, of a matt appearance and lacking in lustre, so that after drying such work is usually polished or buffed with abrasives such as tripoli and rouge. On account of the shortage of trained personnel for this process of polishing, and also because of the economic advantages obtained

thereby, increasing use is being made at the present time of the so-called "bright" plating baths from which plated work may be taken bright and requiring little or no subsequent polishing. For similar reasons there are also employed "electrolytic polishing solutions" in which dull, matt electrodeposits may be rendered bright and highly reflective; in such solutions, which often contain sulphuric acid and orthophosphoric acid, the plated work is made the anode. A summary of some of the chief characteristics of typical plating baths is given in Table 60 on p. 297.

Some typical examples of plating baths are given below—

Cadmium

Cadmium cyanide, $Cd(CN)_2$	41 g
Sodium cyanide	49 g
Water	1 litre

$p_H = 12{\cdot}0 - 13{\cdot}0$

Chromium

Chromic acid, CrO_3	500 g
Sulphuric acid	2·5 g
Water	1 litre

Cobalt

Cobalt sulphate	450 g
Boric acid, H_3BO_3	31 g
Sodium chloride	12·5 g
Water	1 litre

Copper

Copper electrodeposits are widely employed as undercoats for other electrodeposited metals (e.g. nickel and chromium).

(*a*) *Acid sulphate bath*

Copper sulphate	150–200 g
Sulphuric acid	25–37 g
Water	1 litre

The sulphuric acid of this bath improves the electrolytic conductance and prevents rough deposits. The acid sulphate bath is used for electrotyping (or electroforming), that is the reproduction of surfaces for printing processes; for the production of printing rollers employed for the rotary printing of textiles, as well as for the general electrodeposition of copper. This bath however cannot be used for the direct electrodeposition of copper on metals which displace copper from aqueous solutions of copper salts (e.g. iron, steel). For such metals, an initial deposit of copper must first be laid down in the alkaline cyanide bath quoted below, this coating

being followed by deposition of the major portion of the coating in the acid sulphate bath.

(*b*) *Alkaline cyanide bath*

Copper cyanide, CuCN	25 g
Sodium cyanide	37·5 g
Sodium carbonate	12·5 g
Water	1 litre

The "free" cyanide, namely that uncombined with copper as sodium cuprocyanide, $Na_2Cu(CN)_3$, keeps the anode free from insoluble copper cyanide. The chief application of the alkaline cyanide bath is for the electrodeposition of copper on ferrous objects.

(*c*) *Rochelle salt bath*

Copper cyanide, CuCN	28 g
Sodium cyanide	37·5 g
Rochelle salt, $KNaC_4H_4O_6 . 4H_2O$	47 g
Sodium carbonate	15·5 g
Water	1 litre

$p_H = 12·5 - 12·8$

Gold

Metallic gold (as cyanide)	4·2 g
Potassium cyanide	15 g
Water	1 litre

Iron

(*a*) *Chloride bath*

Ferrous chloride, $FeCl_2 . 4H_2O$	300 g
Calcium chloride	335 g
Water	1 litre

(*b*) *Double sulphate bath*

Ferrous ammonium sulphate	350 g
Sulphuric acid	0·25 g
Water	1 litre

Lead

Basic lead carbonate, $Pb(OH)_2 . PbCO_3$	300 g
Hydrofluoric acid (50 per cent)	480 g
Boric acid, H_3BO_3	212 g
Glue	0·2 g
Water	1 litre

Nickel

Watt's type bath

Nickel sulphate, $NiSO_4 . 7H_2O$	105 g
Ammonium chloride	15 g
Nickel chloride, $NiCl_2 . 6H_2O$	15 g
Boric acid, H_3BO_3	15 g
Water	1 litre

$p_H = 5{\cdot}6–5{\cdot}8$

From the Watt's type bath, nickel comes out dull and there are at present in use a number of so-called "bright" nickel plating solutions from which highly lustrous nickel electrodeposits may be obtained.

Platinum

Platinum (as chloride)	5 g
Di-ammonium hydrogen phosphate, $(NH_4)_2HPO_4$	45 g
Disodium hydrogen phosphate, $Na_2HPO_4 . 12H_2O$	240 g
Water	1 litre

Rhodium

(*a*) *Acid sulphate bath*

A solution containing 2 g/litre of metallic rhodium and 20 ml/litre of sulphuric acid.

(*b*) *Acid phosphate bath*

A solution containing 2 g/litre of metallic rhodium and 40 ml/litre orthophosphoric acid.

Rhodium is only applied in the form of extremely thin coatings, usually not more than one millionth of an inch in thickness. This metal is often deposited on top of a silver electrodeposit with the object of preventing the tarnishing of the silver. In appearance, rhodium is similar to silver, but is much harder.

Silver

Silver cyanide, AgCN	40 g
Potassium cyanide	55 g
Potassium carbonate	35 g
Water	1 litre

With the object of obtaining highly lustrous deposits of silver, carbon disulphide is often added to the above bath in small amounts, for example 1/100 fluid ounce per 100 gallons of solution. Silver platings are used not only for decorative purposes, but also as coatings for base metal utensils

for use in the food industries, and on electrical contacts, particularly on radio equipment for use at ultra high frequencies.

Tin

(*a*) *Chloride bath or Alkaline stannite bath*

Stannous chloride, $SnCl_2 . 2H_2O$	30 g
Sodium hydroxide	75 g
Glucose	60 g
Water	1 litre

(*b*) *Alkaline stannate bath*

Sodium stannate, $Na_3SnO_3 . 3H_2O$	80 g
Sodium hydroxide (free)	12 g
Sodium acetate	15 g
Water	1 litre

(*c*) *Acid tin bath*

Stannous sulphate	55 g
Cresol sulphonic acid	100 g
Free sulphuric acid	60 g
Gelatin	2 g
Beta naphthol	1 g
Water	1 litre

Although tin is less protective on steel than either zinc or cadmium—because of its cathodic characteristics relative to the base metal—it is extensively used for the coating of mild steel sheet and an increasing proportion of such tinplate is coated by electrodeposition. Tin is electro-deposited very extensively on non-ferrous alloys such as brass. Kitchen utensils, dairy utensils, refrigerator parts and many domestic utensils are regularly electro-tinned.

Zinc

(*a*) *Sulphate bath*

Zinc sulphate, $ZnSO_4 . 7H_2O$	240 g
Ammonium chloride	15 g
Aluminium sulphate, $Al_2(SO_4)_3 . 18H_2O$	30 g
Water	1 litre

As a brightener, additions of 1 g/litre of liquorice are often made.

(*b*) *Chloride bath*

Zinc chloride	150 g
Sodium chloride	250 g
Aluminium chloride, $AlCl_3 . 6H_2O$	25 g
Water	1 litre
$p_H = 3{\cdot}5–4{\cdot}5$	

(*c*) *Alkaline cyanide bath*

Zinc cyanide, $Zn(CN)_2$	57 g
Sodium cyanide	50 g
Sodium hydroxide	69 g
Water	1 litre

Brass

Copper cyanide, CuCN	21–35 g
Zinc cyanide, $Zn(CN)_2$	63–103 g
Sodium cyanide	83–131 g
Water	1 litre
p_H	10·5–11·5

Bronze. In recent years a copper-tin alloy known as "speculum," containing 55 per cent copper and 45 per cent tin, has become of importance as an electrodeposited coating for tableware, bathroom fittings, jewellery, etc. This alloy has good wearing properties, does not tarnish readily, is unattacked by most foods and has a pleasing appearance. A typical plating bath for this alloy is as follows—

Copper cyanide, CuCN	11 g
Sodium stannate, $Na_2SnO_3 . 3H_2O$	90 g
Sodium hydroxide (free)	15 g
Sodium cyanide (free)	16 g
Water	1 litre

Corrosion

Under certain conditions, metals and alloys are capable of direct chemical attack resulting from which the corrosion product or products accumulate on the surface, becoming thicker and thicker with the passage of time, thus causing the rate of corrosion to become slower and slower. Probably the most common, and the most destructive types of corrosion, however, are those due to electrolytic action. The chief factors influencing this type of corrosion are—

(1) The electrode potential of the metal subjected to attack.

(2) The metal ion concentration in the electrolyte in contact with the metal suffering attack.

(3) The hydrogen ion concentration, that is, the p_H value, of the electrolyte.

(4) The hydrogen overvoltage of the metal.

It is to be emphasized that there are many other factors which have an influence upon metallic corrosion by electrolytic action but probably those enumerated above are the more important.

Dealing with the first factor it will be recalled that those metals exhibiting

electrode potentials which are negative with respect to hydrogen are capable of displacing from aqueous solutions of their salts those metals whose electrode potentials are more positive. Thus iron will displace copper from copper sulphate solution, and zinc will displace silver from silver nitrate solution. These facts become of importance in deciding on suitable protective metallic coatings for those metals less noble than hydrogen. Of particular interest is the case of iron (and of course, steel) for which two metallic coatings, tin and zinc, are widely employed in the commercial production of tinplate and galvanized steel. The normal electrode potentials of iron, zinc and tin are as follows—

Metal	Normal Electrode Potential (volts)
Zinc	— 0·762
Iron	— 0·44
Tin	— 0·136

Thus when imperfect tinplate is exposed to a slightly acidic electrolyte (e.g. rainwater) the galvanic couple established between the steel base and the tin coating is such that the iron behaves as the anode, being higher in the electrochemical series than tin. Current flows therefore from the anodic iron, through the electrolyte to the tin, completing the circuit by flowing from the tin through the metallic interface to the iron (*see* Fig. 123). The net result of this process is the general solution of the iron with the subsequent formation of rust in the presence of air. Imperfections in tinplate therefore tend to grow in size with exposure to electrolytic attack. On the other hand, when imperfect galvanized steel is exposed to similar conditions, the zinc, being slightly higher than iron in the electrochemical series, functions as the anode in the galvanic couple set up and thus the current flow is in the opposite direction to that obtaining in the case of tinplate, that is, as shown in Fig. 124. In other words, zinc tends to be plated out on to the iron exposed at the bottom of the imperfections. This solution of zinc in the neighbourhood of imperfections on galvanized steel is termed *sacrificial corrosion* of zinc.

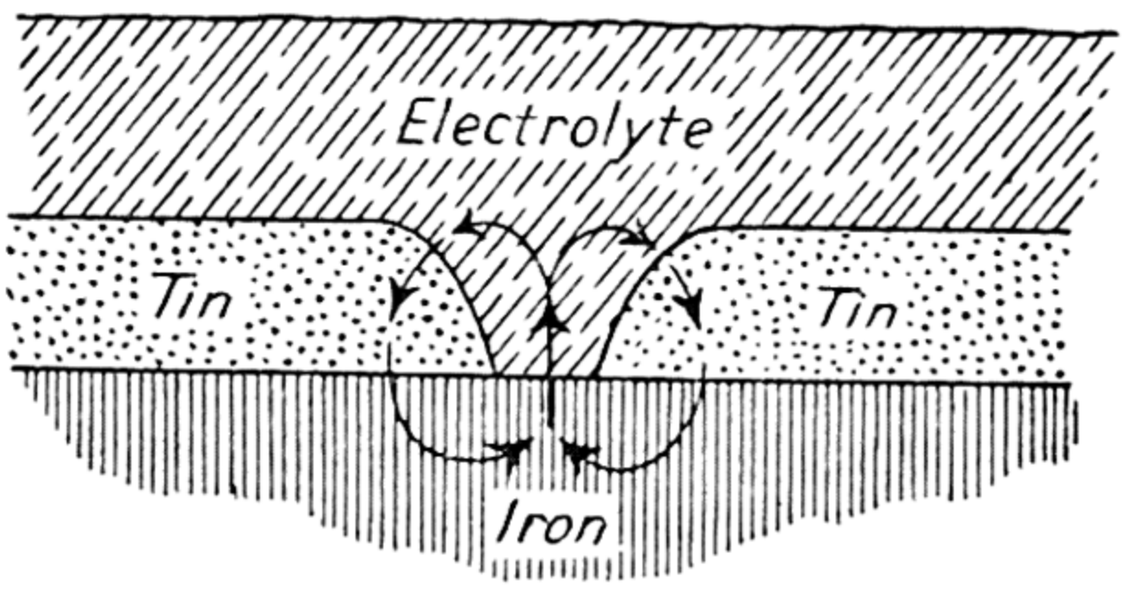


FIG. 123. Corrosion of Imperfect Tinplate

The metal ion concentration in the electrolyte is also of importance in determining the magnitude of electrolytic corrosion since, as the metal ion concentration rises, the electrode potential of that same metal immersed in such an electrolyte becomes less negative, thereby lowering the tendency for corrosion to occur.

With regard to the influence of hydrogen ion concentration upon electrolytic corrosion, it is often the case that with increase in hydrogen ion concentration (i.e. lowering of p_H value) the magnitude of the corrosion is increased.

With respect to the hydrogen overvoltage, it may be said that whenever a metal is in contact with, or has deposited on it, or included within it as a separate phase, a more noble metal exhibiting a small hydrogen overvoltage, then the rate of solution (i.e. corrosion) of the base metal is increased. Thus, *pure* zinc is only attacked slowly by dilute acids, but when such zinc is connected to a piece of copper and both metals are dipped simultaneously into the same dilute acid the rate of solution of the zinc is increased very considerably whilst hydrogen is evolved at the copper which, functioning as a cathode, exhibits a low hydrogen overvoltage of only about 0·2 volt. The same effect is observed when a little copper sulphate is added to a dilute acid in which zinc may be immersed, since copper is deposited at various points on the zinc surface by simple chemical displacement with the result that a large number of local short-circuited galvanic couples are set up. This type of corrosion, which is known as the "hydrogen evolution" type of corrosion, can only occur when the electrode potential of the base metal is more negative than that at which hydrogen evolution, allowing for overvoltage, takes place at the more noble metal. Thus, if the hydrogen ion concentration of the electrolyte is reduced, the potential of the more noble metal is made more negative so that it is sometimes possible to increase the p_H until this particular type of corrosion ceases. If however, the hydrogen is prevented from accumulating at the more positive electrode, the potential of this electrode will assume a more positive value with the result that the rate of solution of the more negative metal will be increased. This condition obtains in the presence of oxygen, which thus functions as a "depolarizer" and oxidizes the hydrogen. In this connexion it is important to appreciate that unless special precautions are taken to exclude air, oxygen is always present during the corrosion of metals. In general, therefore, when two metals in contact are immersed in

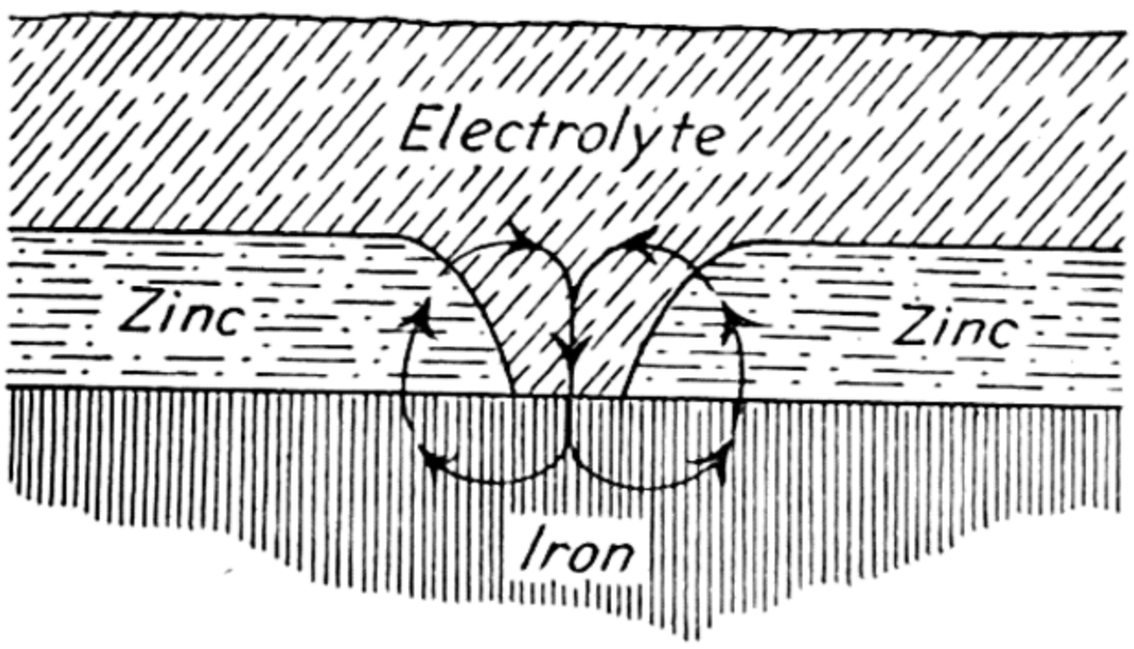


FIG. 124. Corrosion of Imperfect Galvanized Sheet

an electrolyte in the presence of air, the less noble metal will dissolve irrespective of the hydrogen overvoltage at either metal. Thus, reverting to the corrosion of imperfect tinplate, although in the absence of oxygen the high hydrogen overvoltage at tin (0·53 volt) would prevent appreciable anodic solution of the iron, in the presence of air the iron is readily corroded.

The tendency for corrosion to occur is thus increased by the existence of a large potential difference between the two elements of a galvanic couple, and even quite small potential differences are sufficient to cause corrosion in the presence of a depolarizer. Such small potential differences may exist between the various portions of the surface of an apparently uniform piece of metal or alloy; for example, when a polycrystalline mass of pure metal or a solid solution is subjected to mechanical straining, certain portions (i.e. the strained portions) are generally less noble than the unstrained portions so that on immersion of such material in an electrolyte in the presence of a depolarizer there will be established a number of short-circuited galvanic couples.

It is possible even for noble metals to be corroded in the presence of a depolarizer. For example, although copper is not normally regarded as being attacked by cold dilute sulphuric acid, it is dissolved in this acid if air is bubbled through the solution. In actual fact, in acid solution it seems very likely that a very small accumulation of hydrogen must be present on the copper and in the presence of a depolarizer (oxygen in this case) the hydrogen is oxidized as fast as it is discharged with the result that solution of the copper occurs. In a similar manner the vigorous action of nitric acid on copper may be explained as being due to the depolarizing action of the acid; in this case hydrogen is not obtained from the reaction, but reduction products of nitric acid. In the above discussion it has been assumed that the depolarizer is distributed evenly over the surface of the metal. Such a condition however, does not always exist when oxygen is the depolarizer and a type of corrosion known as *differential oxygenation* (or *differential aeration*) may occur. If oxygen is able only to reach certain portions of the surface of a metal, depolarization of hydrogen will occur more readily in these regions which will, therefore, assume a more positive potential than other portions of the metal surface which are not so highly oxygenated. The potential difference thus established leads to corrosion taking place at those parts of the metal surface to which oxygen has not access. Differential oxygenation explains the rusting of iron preferentially under those portions of the surface covered with wet rust; air does not have access to such rust-covered areas which thus become negative in potential with respect to those areas not coated with wet rust.

Differential oxygenation also provides the reason for corrosion of any metal partially covered with a protective film, for example, that at the bottom of "pits" in a metal surface.

The Protection of Metals and Alloys Against Corrosion

In the case of most metals and alloys in everyday use the metallic state is not the most stable; in fact, one may go further and say that those metallic materials which are normally regarded as exhibiting corrosion resistance do so on account of the formation by corrosion of self-formed protective films which in certain cases are so thin as to be invisible to the naked eye, but nevertheless are capable of resisting the penetration of corrosive agencies. Protection against corrosion therefore involves film formation and maintenance in the light of their characteristics, both chemical as well as physical. This is a matter of very considerable economic importance. Such protective films may be formed either by (*a*) a pre-service treatment, or (*b*) by corrosion in its early stages; only the former of these processes will be discussed here.

The chief types of protective films produced by pre-service treatment are as follows—

Chemical compounds such as oxides, phosphates, chromates and sulphides.
Metal coatings.
Paints and varnishes.
Tarry and bituminous mixtures.
Vitreous enamels and glass.
Rubber.
Cement and concrete.
Greases and oils.

Chemical Compounds

Iron and Steel. The formation of oxide coatings by the low temperature heat-treatment process of tempering, involving heating in air at temperatures of 200°–400°C, confers a perceptible degree of corrosion resistance to iron and steel components. Similarly, when ferrous components are heated, as in the Bower-Barff process, at approximately 800°C first in air, then in steam and finally in producer gas, there results the formation of a highly durable coating of ferroso-ferric oxide, Fe_3O_4. Other oxide-forming processes involve the immersion of the work in hot aqueous solutions of caustic alkali and alkaline metal nitrates. More satisfactory than the above oxide coatings from the point of view of resistance to corrosion are the phosphate coatings produced by immersion of the steel in hot or boiling solutions containing phosphates. Resulting from such treatment slightly soluble films of iron phosphates are deposited on the metal surface. Such phosphate treatment has been modified in many ways as in various patented processes such as Coslettizing, Parkerizing, Granodizing, Bonderizing and Walterization. The natural colour of phosphate-treated work is grey, although good black finishes may be obtained by impregnation of the coating with black dye. Protection against corrosion is only of

a moderate order, but it may be improved by the application of oil, grease, paint, or varnish. In general, the protection afforded by the phosphate-paint treatments against corrosion of steel under severe conditions, such as sea spray, is not as high as that obtained by electrodeposited coatings of cadmium or of zinc of 0·0003 in.–0·0005 in. in thickness.

Aluminium and its Alloys. Aluminium and its alloys are extensively treated by the process known as "anodizing" (*see* p. 546) resulting from which a film of alumina is produced electrolytically.

Copper and its Alloys. Although the resistance to corrosion of copper may be slightly enhanced by heating the metal to 75°–100°C in clean air to form an oxide film, this process is not so widely practised as are immersion processes giving rise to the production of sulphide films. Thus, the immersion of copper and its alloys (e.g. brass) in aqueous solutions of such compounds as alkali sulphide, ammonium polysulphides, and sodium thio-antimonate in the presence of air results in the formation of brown sulphide films, often erroneously referred to as "oxidized" films.

The green patina consisting very largely of basic cupric sulphate, $CuSO_4 . 3Cu(OH)_2$, developed on the surface of old copper, particularly sheet copper on roofs after prolonged ageing in the atmosphere, has enabled such copper to give a useful life over several centuries. This patina may be produced artificially either by direct immersion in suitable baths or alternatively by anodic treatment of the metal in a solution containing 10 per cent magnesium sulphate, 2 per cent magnesium hydroxide, and 2 per cent potassium bromate. The bath temperature is maintained at approximately 95°C, and the current density is approximately 0·5 amp/ft^2, the treatment time being fifteen minutes.

Cadmium. The corrosion resistance of cadmium may be improved by the presence of films of sulphur-containing compounds produced by immersion of the work in a mixed aqueous solution of lead acetate and sodium thiosulphate.

Zinc. Zinc may be treated in phosphate-containing solutions to give a coating of zinc phosphate. The Granodine and the Lithoform treatments are patented processes of this type.

The resistance to corrosion of zinc may also be enhanced by the formation of chromate films produced by immersion of either zinc or zinc plated work in a mixed aqueous solution of sodium dichromate and sulphuric acid; of such a nature is the Cronak process. This so-called *chromate passivation* is of considerable value in preventing the formation of white corrosion products of basic zinc salts under conditions of humidity. This process is of chief application to those components subject to condensation and humidity, but protected from the outside weather.

Magnesium Alloys. Magnesium alloys are treated either by anodic treatment in a mixed aqueous solution of sodium dichromate, potassium permanganate and sodium hydroxide; or alternatively simply by immersion

for thirty minutes in a boiling aqueous solution containing ammonium sulphate, ammonium dichromate, potassium dichromate and ammonium hydroxide.

Metal Coatings

Metal coatings may be laid down on base metals in various ways as detailed below.

Hot-dipped Coatings. Steel is regularly coated with zinc by the process of galvanizing; this process is applied to sheet, wire and netting, as well as to irregularly-shaped articles. The work is first pickled in dilute sulphuric acid, washed with water, pickled in dilute hydrochloric acid, washed, dried, and then immersed in a bath of molten zinc maintained at a temperature of approximately 450°C.

Hot-tinning is conducted on mild steel, cast iron and copper; sheet and wire are immersed in the molten tin bath by mechanical means, whilst irregularly shaped articles are immersed by hand. The temperature of the tin bath is 310°–345°C.

Lead coatings provide a comparative immunity to attack by sulphuric acid and sulphurous acid. The work is first pickled and then treated as in the case of zinc and tin. Steel is also hot-dipped to produce *terne plate* by immersion in a molten alloy containing 75 per cent lead and 25 per cent tin.

Hot-dipped aluminium-coated steel sheet is also in commercial production.

Electrodeposited Coatings. The production of metal and alloy coatings by electrodeposition has already been discussed previously (*see* p. 295).

Metallization. Metal coatings are laid down on base metals, particularly on iron and steel, by metal spraying. The protecting metal, fed into a special type of pistol either in the form of a powder or a wire, is melted by a high-temperature oxy-fuel gas flame and blown in the form of an extremely finely divided cloud of metal droplets on to the base metal to which it bonds and forms the protective coating. Most pure metals and a number of alloys may be applied by metallization.

Cementation. Cementation involves the heating of the component to be protected in a dust of the protecting metal. During this heating, alloying occurs between the base metal and the protecting metal even though the melting point of the latter has not been attained during heating. The film produced is not homogeneous in composition, but decreases in content of the protecting metal with penetration downwards from the surface.

Sherardizing is the process of heating steel objects in zinc dust at a temperature of 350°–367°C. A coating thickness of 0·0003 in.–0·0005 in. is normally attained.

Chromizing is the process of heating steel objects in a mixture of 55 per

cent chromium powder and 45 per cent alumina at a temperature of 1300°–1400°C.

Calorizing involves the heating of work in a mixture of aluminium powder and alumina at a temperature of 900°–950°C for iron and steel, and 700°–800°C for copper and brass. Alumina prevents the coalescence of the aluminium globules.

The Follsain process is similar.

Mechanically Applied Metal Coatings. Such coatings may be applied by the simultaneous rolling of a thin sheet of the protecting metal with the base metal at a temperature sufficiently high to permit of welding of the two metals (or metal and alloy). Included in this category are such products as "Alclad," consisting of a coating of pure aluminium rolled on to duralumin (*see* p. 546), and nickel-clad steel. Alternatively, the protecting metal may be cast as a shell around a billet of the base metal and the composite billet which results rolled out into sheet form. An example of such material is copper-clad steel plate.

Paints and Varnishes

Paints may be defined as being viscous suspensions of finely divided solid pigments in a fluid medium consisting of driers, the whole being capable on exposure to the air of producing films exhibiting protecting power and hiding or obliterating power. There are many pigments employed amongst which may be mentioned red lead, white lead, lithopone, lead chromate, zinc chromate and zinc oxide; from the point of view of enhancing resistance to corrosion it may be said that in general the most effective pigments are those of an oxidizing nature such as red lead, lead chromate and zinc chromate; these pigments tend to give rise to the formation of thin protective oxide films.

Varnishes are made by dissolving either natural or synthetic resins in oils (e.g. linseed and tung oils) or in spirits (e.g. methyl and ethyl alcohols, turpentine, naphtha, and petroleum spirit).

Tarry and Bituminous Mixtures

For the protection of buried gas and water mains and the protection of structural steelwork under highly corrosive conditions (e.g. in chemical works and gas works) coatings of tarry and bituminous mixtures are often employed.

Vitreous Enamels and Glass Linings

Fused coatings of vitreous enamels are widely employed as protective coatings on objects fabricated from iron and steel. Such vitreous enamels are complex mixtures of metallic silicates. They find considerable application for kitchen utensils, domestic cookers and washers, and for bathroom equipment.

In the chemical industries plant made from metals and alloys is being provided with glass linings in increasing degree.

Rubber

Chemical plant is often lined with rubber as an aid to improving resistance to corrosion. In particular, this material has become a very effective lining material for acid pickling tanks.

Cement and Concrete

Cement and concrete find application as protective linings for large steel mains where the effluent to be carried is of a corrosive nature. Various special compositions have been developed for such purposes.

Greases and Oils

Possibly the most common of all films applied to metals with the object of preventing or minimizing corrosion are films of greases and oils. These materials are in such common and wide application that little needs to be said here.

CHAPTER 13

EQUILIBRIA IN ELECTROLYTES

IN a solution of an electrolyte a condition of equilibrium exists between the free ions and the undissociated molecules, these latter consisting either of ion pairs or alternatively of non-ionized molecules. Thus such an equilibrium may be expressed as—

$$AB \rightleftharpoons A^+ + B' \quad . \quad . \quad . \quad . \quad (1)$$

To this system in equilibrium the Law of Mass Action may be applied.

THE APPLICATION OF THE LAW OF MASS ACTION

If one gramme molecule of the binary electrolyte AB is dissolved in V litres of solution, and the fraction AB dissociated at this dilution is α, then the non-dissociated fraction will be $1 - \alpha$. Therefore, at equilibrium, the concentration in gramme molecules/litre of AB A^+ and B' will be—

$$\frac{1-\alpha}{V} \text{ of } AB, \quad \frac{\alpha}{V} \text{ of } A^+, \quad \text{and } \frac{\alpha}{V} \text{ of } B'$$

therefore, applying the Law of Mass Action—

$$\frac{\left(\frac{\alpha}{V}\right) \times \left(\frac{\alpha}{V}\right)}{\left(\frac{1-\alpha}{V}\right)} = K$$

or,

$$\frac{\left(\frac{\alpha}{V}\right)^2}{\left(\frac{1-\alpha}{V}\right)} = K \quad . \quad . \quad . \quad . \quad (2)$$

from which,

$$\frac{\alpha^2}{(1-\alpha)V} = K \quad . \quad . \quad . \quad . \quad (3)$$

or, alternatively,

$$\frac{c\alpha^2}{(1-\alpha)} = K \quad . \quad . \quad . \quad . \quad (3a)$$

where

$$c = \text{concentration} = \frac{1}{V} \text{ (gramme molecules/litre)}$$

Equation (3) expressing the relationship between the degree of dissociation of an electrolyte and its dilution is the mathematical form of *Ostwald's Dilution Law*, and the constant, K, the *dissociation constant* or the *affinity constant*; this constant is characteristic of every electrolyte.

The conductance ratio, Λ_c/Λ_0 (*see* p. 254), was long regarded as being identical with α, the degree of dissociation. In the case of weak electrolytes over an appreciable concentration range this statement is approximately true so that on introducing values for α in equation (3) the numerical value of K may be calculated. In the case of acetic acid some typical values are quoted in Table 61; it should be noted that the acetic acid solutions are reported in terms of differing concentrations. As is to be expected the value of α decreases with increasing concentration, or increases with increasing dilution.

TABLE 61

Application of the Ostwald Dilution Law to Acetic Acid at 25°C

($\Lambda_0 = 390{\cdot}6$ *reciprocal ohms at 25°C*)

Concentration (mols per litre of Electrolyte)	Λ_c (reciprocal ohms)	Λ_c/Λ_0	K
$0{\cdot}11135 \times 10^{-3}$	127·710	0·3195	$1{\cdot}744 \times 10^{-5}$
$0{\cdot}2184 \times 10^{-3}$	96·406	0·2468	$1{\cdot}767 \times 10^{-5}$
$1{\cdot}0283 \times 10^{-3}$	48·133	0·1232	$1{\cdot}781 \times 10^{-5}$
$2{\cdot}4140 \times 10^{-3}$	32·208	0·8025	$1{\cdot}789 \times 10^{-5}$
$5{\cdot}9115 \times 10^{-3}$	20·956	0·0537	$1{\cdot}799 \times 10^{-5}$
$12{\cdot}829 \times 10^{-3}$	14·371	0·0368	$1{\cdot}803 \times 10^{-5}$
$20{\cdot}000 \times 10^{-3}$	11·563	0·0296	$1{\cdot}806 \times 10^{-5}$
$50{\cdot}000 \times 10^{-3}$	7·356	0·0188	$1{\cdot}808 \times 10^{-5}$

From Table 61 it will be noted that for acetic acid solutions over a considerable concentration range, Ostwald's Dilution Law is approximately true; this statement also holds for a large number of weak electrolytes, both bases as well as acids. In the case of such weak electrolytes the numerical value of the dissociation constant K gives a very useful measure of the strength of the electrolyte under investigation.

Equation (3) may be rewritten—

$$\alpha^2 = KV(1 - \alpha) \quad . \quad . \quad . \quad . \quad (4)$$

and since for most weak electrolytes at moderate dilutions the value of α is very small, equation (4) may be simplified thus—

$$\alpha^2 = KV$$

so that

$$\alpha = \sqrt{KV} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From which it follows that the "strength" of a weak electrolyte is proportional to the square root of its dissociation constant. Divalent and polyvalent acids (and also bases) have two or more dissociation constants which often have widely differing values. For example orthophosphoric acid, H_3PO_4, a trivalent acid, has three dissociation constants, $K_1 = 1 \times 10^{-2}$, $K_2 = 2 \times 10^{-7}$, and $K_3 = 4 \times 10^{-12}$.

The Anomaly of Strong Electrolytes. It is an experimental fact that the stronger the electrolyte the more pronounced does its dissociation constant depart from constancy with variation of dilution. This fact may be illustrated by reference to data for potassium chloride, a typical strong electrolyte, as given in Table 62.

TABLE 62

Conductance Ratios and Dissociation Constants for Aqueous Solutions of Potassium Chloride

Dilution of Solution (in litres)	$\alpha = \Delta_v/\Delta_\infty$	K (As calculated from Ostwald's Dilution Law)
10	0·861	0·533
20	0·888	0·352
50	0·922	0·218
100	0·943	0·156
200	0·961	0·118

From time to time, various empirical formulae have been proposed in an effort to equate the degree of dissociation and the concentration of a solution of a strong electrolyte. Thus, Kohlrausch suggested that,

$$1 - \alpha \propto \sqrt{C} \quad . \quad . \quad . \quad . \quad (6)$$

where C is the concentration, and α, the degree of dissociation, is small. It is, however, now generally realized that some confusion has arisen in the past by assuming that the concentration and the activity of an electrolyte are identical. In the case of weak electrolytes, particularly in solutions of low concentration, there is little difference between the activity and the concentration of the solute, and as has been shown for acetic acid in Table 61, Ostwald's Dilution Law is obeyed over a considerable concentration range. In the case of strong electrolytes, however, the conductance ratio is not a satisfactory index of the degree of dissociation, in addition to which it should be borne in mind that the activities and the concentrations of the different species are probably very different.

Debye and Hückel (1923) have proposed that the variations in the equivalent conductance of a solution of an electrolyte are due to changes in the mobility of the ions rather than to changes in their number. In a solution of an electrolyte, Debye and Hückel have suggested that there exists an oppositely charged ionic "atmosphere" surrounding each ion; in other words, there is an excess of negative ions in the neighbourhood of a positive ion, and likewise an excess of positive ions in the neighbourhood of a negative ion. The mobility of ions is therefore influenced in two ways. The oppositely charged ionic atmosphere lags behind an ion moving through a solution and thus, by virtue of its electrostatic attractive force has a retarding effect upon the moving ion; and, in addition, a moving ion encounters increased frictional resistance on dragging its ionic atmosphere through a solution. Debye and Hückel were able to give mathematical interpretation to these phenomena and showed that together these retardations were proportional to the square root of the concentration of the electrolyte.

Although the Debye-Hückel theory was developed primarily to help in solving the anomaly of strong electrolytes, the interionic action effects are exhibited by all electrolytes, both weak and strong, but since in the case of weak electrolytes the ionic concentration is very small, the retardation effect is too small to be of any significance; in other words, the Ostwald Dilution Law is obeyed.

ACIDS AND BASES

As far as aqueous solutions are concerned an acid may be defined as a substance which yields hydrogen ions, whilst a base is a substance which yields hydroxyl ions, but when non-aqueous solvents are involved these definitions are inadequate, so that in general it is preferable to define an acid as a substance exhibiting a tendency to lose a proton, and a base as a substance capable of accepting a proton.

If an acid is represented by the symbol A and its *conjugate* base by the symbol B, their relationship may be expressed in equation form as follows—

$$\underset{\text{acid}}{A} \rightleftharpoons \underset{\text{proton}}{H^+} + \underset{\text{base}}{B} \quad . \quad . \quad . \quad . \quad (7)$$

Since in solution free protons are probably incapable of free existence, the acid or the basic characteristics of any ionic species are not evident unless the solvent itself is capable of accepting, or alternatively of yielding protons; in other words, the solvent itself must exhibit either basic or, alternatively, acidic characteristics.

Solvents capable of accepting protons are said to be *protophilic* (i.e. basic in character) whilst solvents capable of yielding protons are termed *protogenic* (i.e. acidic in character). There also exist certain solvents which

are neither proton acceptors nor proton donors; such substances are said to be *aprotic* solvents.

Good examples of protophilic solvents are provided by water and the alcohols on account of the fact that the oxygen atom present in the molecule readily accepts a proton. If the solvent is designated R.OH, in which R may be a hydrogen atom, the condition of equilibrium existing when an acid is present may be depicted thus—

$$\underset{\text{acid}}{HA} + \underset{\substack{\text{solvent}\\(\text{basic in nature})}}{R.OH} \rightleftharpoons \underset{\text{acid}}{R.OH_2^+} + \underset{\text{base}}{A'} \quad . \quad . \quad . \quad (8)$$

In such solutions the substance $R.OH_2^+$ is termed the *hydrogen ion*, and in aqueous solution this entity corresponds to the *hydroxonium ion*, H_3O^+.

Although it is often convenient when using different solvents to represent the hydrogen ion by the symbol H^+, it should be borne in mind that the actual ions are different for differing solvents. The stronger the protophilic character of the solvent the more completely reaction (8) goes from left to right. Thus, in aqueous solutions, strong acids (except in very concentrated solutions) will behave as though they are all equally strong acids since the basic character of water results in almost complete conversion into H_3O^+ ions, and the strengths of such solutions cannot be distinguished.

In a protogenic solvent (e.g. HF or HCl) which exhibits no basic characteristics, even the strongest acid is incapable of exhibiting acid properties since there are no molecules available to accept protons. In an aprotic solvent (e.g. a hydrocarbon) neither acidic nor basic properties are exhibited. The more protogenic (i.e. the more acidic) the solvent the more readily will the properties of a base become evident. In acetic acid, for example, all bases stronger than aniline appear equally strong.

Water and the alcohols are also said to be *amphiprotic* in that they are capable of exhibiting protogenic as well as protophilic characteristics. The base-solvent equilibria in the case of such solvents may therefore be represented as—

$$\underset{\text{base}}{B} + \underset{\substack{\text{solvent}\\(\text{acidic in}\\\text{character})}}{R.OH} \rightleftharpoons \underset{\text{acid}}{BH^+} + \underset{\text{base}}{OH'} \quad . \quad . \quad . \quad (9)$$

Therefore, with water as solvent all strong bases exist more or less completely as OH' ions.

Summarizing then, for aqueous solutions, strong acids are converted into hydroxonium ions, H_3O^+, whilst strong bases are converted into hydroxyl ions, OH'. The strengths of acids are proportional to the hydrogen ion concentrations of their solutions, and, therefore are measured by the numerical value of their dissociation constants. Similarly, the strengths of bases are proportional to their dissociation constants.

The Ionic Product of Water. The neutralization of hydrochloric acid by sodium hydroxide is depicted by the following chemical equation—

$$HCl + NaOH = NaCl + H_2O \quad . \quad . \quad . \quad (10)$$

This equation may be rewritten ionically as follows—

$$H^+ + Cl' + Na^+ + OH' = Na^+ + Cl' + H_2O \quad . \quad . \quad (11)$$

Examination of equation (11) shows that chlorine ions and sodium ions are common to both sides of the equation, so that this ionic equation may be rewritten—

$$H^+ + OH' = H_2O \quad . \quad . \quad . \quad . \quad (12)$$

From equation (12) it would appear that the neutralization of an acid by a base consists of nothing more nor less than the formation of water from its ions. If an examination is made of the changes occurring when any other strong acid is neutralized by a strong base the same result will be obtained. Further evidence of this phenomenon is provided by the fact that the heat of neutralization of a strong acid by a strong base is always in the region of 13 700 g.cal/g. equivalent.

From experimental evidence regarding the electrical conductivity of very pure water, reaction (12) may be regarded as reversible—

$$H^+ + OH' \rightleftharpoons H_2O \quad . \quad . \quad . \quad . \quad (13)$$

Applying the Law of Mass Action to equation (13) above—

$$[H^+]\,[OH'] = K[H_2O] \quad . \quad . \quad . \quad . \quad (14)$$

But since it has been shown that the dissociation into ions is only slight, in other words the amount of undissociated water is so considerable that it can be regarded as constant, equation (14) may be simplified to—

$$[H^+]\,[OH'] = K_w \quad . \quad . \quad . \quad . \quad (15)$$

where K_w is a constant known as the *ionic product* for water. Since the conductivity of water increases with rising temperature, the corresponding value of K_w will also increase; values of K_w at various temperatures are given in Table 63.

In actual fact the reaction taking place in water is as follows—

$$\overset{\swarrow H^+ \nwarrow}{H_2O + H_2O} \rightleftharpoons H_3O^+ + OH' \quad . \quad . \quad . \quad (16)$$

The H_2O molecular groups constituting water are in constant agitation, their energy of movement being determined by the temperature. When two such groups are in collision a proton is transferred from one to the other. One molecular group thus acquires a positive charge and

becomes the hydroxonium ion, H_3O^+ whilst the other, having lost a proton, becomes a hydroxyl ion, OH'.

TABLE 63

Variation of the Ionic Product for Water with Temperature

Temperature (°C)	Ionic Product (K_w)
0	$0{\cdot}11 \times 10^{-14}$
10	$0{\cdot}29 \times 10^{-14}$
25	$1{\cdot}01 \times 10^{-14}$
40	$2{\cdot}92 \times 10^{-14}$
50	$5{\cdot}48 \times 10^{-14}$
100	$(56) \times 10^{-14}$

It is important to note that each hydroxonium ion is accompanied by a hydroxyl ion, so that in neutral solution the concentrations (or to be more precise the activities) of these two ions are equal, and therefore from equation (15) each of these concentrations is equal to $\sqrt{K_w}$. Therefore, if the round figure of 1×10^{-14} be taken for K_w at 25°C, then the concentrations of the hydroxonium and the hydroxyl ions are 1×10^{-7} g ions per litre. It is common usage, as was suggested earlier, to speak of the hydrogen ion concentration when in actual fact the hydroxonium ion concentration is the true statement of the fact; the usual terminology will be employed here.

Hydrogen Ion Concentration. If the hydrogen ion concentration exceeds the value of 1×10^{-7} g ions per litre (i.e. that existing in pure water), the solution is said to be acidic; in such a solution the concentration of hydroxyl ions must be less than 1×10^{-7} g ions per litre if equation (15) is taken to be valid. Similarly, in alkaline solutions the hydrogen ion concentration must be less than 1×10^{-7} g ions per litre and the concentration of hydroxyl ions greater than 1×10^{-7} g ions per litre. Thus, if the concentration of either hydrogen ions or of hydroxyl ions is known, the value of the other may be evaluated.

It is usually more convenient to express hydrogen ion concentration in terms of a scale originally suggested by Sørensen (1909) in which the negative logarithm of the hydrogen ion concentration is known as the pH (or p_H) of the solution. In mathematical form—

$$p\mathrm{H} = -\log_{10}[\mathrm{H}^+] \quad . \quad . \quad . \quad . \quad (17)$$

or,

$$[\mathrm{H}^+] = 10^{-p\mathrm{H}}$$

and, since the ionic product for water is 1×10^{-14} (at 25°C) therefore,

$$\log \frac{1}{[H^+]} + \log \frac{1}{[OH']} = 14 \quad . \quad . \quad . \quad (18)$$

Therefore, $$pH + pOH = pK_w = 14 \quad . \quad . \quad . \quad (19)$$

Thus, as *p*H values diminish below *p*H 7, solutions become increasingly acidic; *p*H 7 represents neutrality, and as *p*H values rise above *p*H 7, solutions become progressively more and more alkaline.

The Calculation of Hydrogen Ion Concentration

(1) An N/100 (i.e. 0·01 N) solution of hydrochloric acid contains 0·01 g hydrogen ions per litre (ignoring the consideration of activity coefficients); that is 1×10^{-2} g hydrogen ions per litre.

∴ the *p*H value of this solution is 2.

(2) Suppose it is required to calculate the *p*H value of a solution which is $3{\cdot}62 \times 10^{-3}$ N with respect to hydrogen ions.

The *p*H value is numerically equal to the logarithm of the reciprocal of the hydrogen ion concentration,

i.e. $$pH = -\log [H^+]$$

But
$$\log [H^+] = \log (3{\cdot}62 \times 10^{-3})$$
$$= 0{\cdot}5587 + (-3{\cdot}0)$$
$$= -2{\cdot}4413$$

∴ $$pH = 2{\cdot}4413$$

(3) If the *p*H value of a solution is 6·35 the actual value of the hydrogen ion concentration may be calculated as follows—

Given that *p*H value $= 6{\cdot}35$

This implies that the hydrogen ion concentration $= 1 \times 10^{-6{\cdot}35}$

The exponent, $-6{\cdot}35 = -10 + 3{\cdot}65$

Therefore, $10^{-6{\cdot}35} = 10^{-10} + 10^{3{\cdot}65}$

From tables, the antilog of 3·65 $= 2317$

Therefore, $pH = 6{\cdot}35 \equiv 2317 \times 10^{-10}$ g ions per litre

$= 2{\cdot}317 \times 10^{-7}$ g ions per litre

HYDROLYSIS

If an aqueous solution of a strong acid is added to the aqueous solution of a strong alkali of equivalent concentration, a neutral salt is formed. In words, the chemical equation may be written—

$$\text{Acid} + \text{Base} = \text{Salt} + \text{Water} \quad . \quad . \quad . \quad (20)$$

If the acid were hydrochloric acid and the base sodium hydroxide the reaction may be written ionically thus—

$$H^+ + Cl' + Na^+ + OH' = Na^+ + Cl' + H_2O \quad . \quad . \quad (21)$$

The hydrogen ions and the hydroxyl ions interact until there is no excess of either and the *p*H of the resulting solution is 7·0. In other words, the solution which results will be neutral. It is a well-known fact, however, that the aqueous solutions of a large number of salts exhibit not a neutral reaction, but either an alkaline or an acidic reaction. This phenomenon, known as *hydrolysis*, is due to the interaction of a salt with water; in effect it may be regarded as a reverse of neutralization so that equation (20) may be rewritten thus—

$$\text{Salt} + \text{Water} \rightleftharpoons \text{Acid} + \text{Base} \quad . \quad . \quad . \quad (22)$$

This effect, however, is only observed when either the acid and the base involved are of unequal strengths, or both acid and base are weak. The cause of hydrolysis is due to the slight dissociation of water leading to the formation of a minute concentration of hydrogen ions and of hydroxyl ions; this *slight* dissociation may be depicted in equation form as follows—

$$H_2O \rightleftharpoons H^+ + OH' \quad . \quad . \quad . \quad . \quad (23)$$

In discussing the phenomenon of hydrolysis in detail three types of salts will be considered—

(1) Salts of weak acids and strong bases.
(2) Salts of strong acids and weak bases.
(3) Salts of weak acids and weak bases.

Salts of Weak Acids and Stong Bases. To illustrate this particular case, sodium carbonate will be used as an example. In aqueous solution this salt is dissociated as depicted in equation (24) below—

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3'' \quad . \quad . \quad . \quad (24)$$

The feeble dissociation of water is represented as in equation (23) above, i.e.—

$$H_2O \rightleftharpoons H^+ + OH'$$

There are therefore in the solution four different ions—hydrogen ions, hydroxyl ions, sodium ions and carbonate ions. The sodium ions are able to combine with the hydroxyl ions to form sodium hydroxide, but since this substance is a strong base there are immediately reformed sodium ions and hydroxyl ions so that the final condition with regard to these two ions remains unchanged. On the other hand, the carbonate ions are able to combine with the hydrogen ions to form carbonic acid, H_2CO_3. Carbonic acid is, however, a weak acid—in other words, is only feebly dissociated; this may be depicted as shown in equation (25)—

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3'' \quad . \quad . \quad . \quad (25)$$

Thus hydrogen ions are removed and more molecules of water must dissociate to maintain the ionic product for water at a constant value. There is, therefore, a competition for the possession of hydrogen ions between the carbonate ions and the hydroxyl ions; ultimately a condition of equilibrium is attained depending upon the relative tendencies of the carbonic acid and water to undergo dissociation. Thus, the concentration of hydroxyl ions in the solution will exceed that of the hydrogen ions since some of these latter ions have been used up in forming undissociated molecules of carbonic acid.

The net result of these processes, which are proceeding simultaneously, may be represented thus—

$$Na_2CO_3 + 2H_2O \rightleftharpoons \underset{\text{a strong base, therefore strongly dissociated yielding a high concentration of hydroxyl ions}}{2NaOH} + \underset{\text{a weak acid, therefore feebly dissociated yielding a low concentration of hydrogen ions.}}{H_2CO_3} \quad . (26)$$

Other examples of the production of such alkalinity in aqueous solution are provided by the alkali salts of acetic acid, boric acid, phosphoric acid, hydrocyanic acid, hydrosulphuric acid and hypochlorous acid.

Modifying equation (26) for the general case where MA is the salt of the weak acid HA and the strong base MOH—

$$MA + H_2O \rightleftharpoons MOH + HA \quad . \quad . \quad . (27)$$

or,

$$\underbrace{M^+ + A'}_{\text{salt}} + H_2O \rightleftharpoons \underbrace{M^+ + OH'}_{\text{strong base}} + \underset{\text{acid}}{\underset{\text{weak}}{HA}} \quad . \quad . (28)$$

Applying the Law of Mass Action to equation (28)—

$$\frac{[M^+]\,[OH']\,[HA]}{[M^+]\,[A']\,[H_2O]} = K_H \quad . \quad . \quad . \quad . (29)$$

where K_H is the so-called *hydrolysis constant* of the salt.
But since

$$\frac{[H^+]\,[A']}{[HA]} = K_{HA} \text{ (dissociation constant of the acid)} \quad . (30)$$

introducing (30) in equation (29), and omitting water, since its concentration may be assumed to be constant in dilute solution—

$$\frac{[M^+]\,[OH']\,[H^+]\,[A']}{[M^+]\,[A']K_{HA}} = K_H \quad . \quad . \quad . (31)$$

which may be simplified to—

$$\frac{[OH'][H^+]}{K_{HA}} = K_H \quad . \quad . \quad . \quad . \quad (32)$$

Since $[OH'][H^+] = K_w$ (the ionic product for water) . . (15)

it follows that—

$$\frac{K_w}{K_{HA}} = K_H \quad . \quad . \quad . \quad . \quad (33)$$

or, in words, the hydrolysis constant K_H is proportional to the ionic product for water and inversely proportional to the dissociation constant for the weak acid involved.

It should be carefully noted that K_H is the hydrolysis constant and not the degree of hydrolysis, although the latter may be calculated from the hydrolysis constant as follows.

If 1 g.mol of a salt MA is dissolved in V litres of water, and if h represents the degree of hydrolysis (i.e. the fraction of the total salt hydrolyzed), then at equilibrium there will be $(1-h)/V$ g.mol. of unhydrolyzed salt, h/v g.mol. of the acid HA, and h/V g.mol. of the base MOH—

$$\underset{\frac{1-h}{V}}{MA} + H_2O \rightleftharpoons \underset{\frac{h}{V}}{MOH} + \underset{\frac{h}{V}}{HA} \quad . \quad . \quad . \quad (34)$$

Therefore, applying the Law of Mass Action—

$$\frac{\left(\frac{h}{V}\right)\left(\frac{h}{V}\right)}{\left(\frac{1-h}{V}\right)} = K_H \quad . \quad . \quad . \quad . \quad (35)$$

$$= \frac{\left(\frac{h}{V}\right)^2}{\left(\frac{1-h}{V}\right)} = K_H \quad . \quad . \quad . \quad . \quad (36)$$

$$= \frac{h^2}{V(1-h)} = K_H \quad . \quad . \quad . \quad . \quad (37)$$

If the value of h is small, then equation (37) may be simplified thus—

$$h^2 = VK_H \quad . \quad . \quad . \quad . \quad (38)$$

Therefore

$$h = \sqrt{VK_H} \quad . \quad . \quad . \quad . \quad (39)$$

Taking as a specific example, a normal solution of sodium acetate; the dissociation constant of acetic acid is $1{\cdot}8 \times 10^{-5}$, and taking the value of K_w to be $1{\cdot}0 \times 10^{-14}$, then—

since
$$K_{\mathrm{H}} = \frac{K_w}{K_{\mathrm{HA}}}$$
$$= \frac{1{\cdot}0 \times 10^{-14}}{1{\cdot}8 \times 10^{-5}}$$
$$= 5{\cdot}555 \times 10^{-10}$$

In a normal solution, the numerical value of V in equation (39) is 1, therefore,

$$h = \sqrt{1 \times 5{\cdot}555 \times 10^{-10}}$$
$$= 2{\cdot}36 \times 10^{-5}$$
$$= 0{\cdot}00236$$

From equation (37) above it follows that the degree of hydrolysis increases with increasing dilution.

Salts of Strong Acids and Weak Bases. Salts of strong acids and weak bases hydrolyze in aqueous solution to give an acidic reaction. Taking ferric chloride as an example, this salt dissociates as indicated in equation (40)—

$$\mathrm{FeCl_3} \rightleftharpoons \mathrm{Fe^{+++}} + 3\mathrm{Cl'} \quad . \quad . \quad . \quad (40)$$

and the feeble dissociation of water is represented as in equation (23) by

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH'}$$

There are therefore in the solution four different ions, hydrogen ions, hydroxyl ions, ferric ions and chlorine ions. The chlorine ions are capable of combining with the hydrogen ions to form hydrochloric acid, but since this compound is a very strong acid there are immediately reformed hydrogen ions and chlorine ions, thus, the final condition is that these two ions remain unchanged. On the other hand, however, the ferric ions are able to combine with the hydroxyl ions to form ferric hydroxide, a weak base which is therefore only feebly dissociated as depicted in equation (41)

$$\mathrm{Fe^{+++}} + 3(\mathrm{OH'}) \rightleftharpoons \mathrm{Fe(OH)_3} \quad . \quad . \quad . \quad (41)$$

The net result is that hydroxyl ions are removed and more molecules of water must dissociate to maintain the ionic product for water at a constant value. In this case there is a competition for the possession of the hydroxyl ions between the hydrogen ions and the ferric ions until finally a condition of equilibrium is attained depending upon the relative tendencies for the ferric hydroxide and the water to dissociate.

At equilibrium, therefore, the concentration of the hydrogen ions in the

solution will exceed that of the hydroxyl ions since some of the latter have been used up in forming undissociated ferric hydroxide. These processes, which are proceeding simultaneously, may be represented thus—

$$FeCl_3 + 3H_2O \rightleftharpoons \underset{\substack{\text{a weak base, therefore feebly dissociated, yielding a low concentration of hydroxyl ions}}}{Fe(OH)_3} + \underset{\substack{\text{a strong acid, therefore strongly dissociated, yielding a high concentration of hydrogen ions}}}{3HCl} \quad . \quad . \quad (42)$$

Aqueous solutions of ferric chloride therefore give an acidic reaction.

Other examples of salts of strong acids and weak bases which, in aqueous solution behave similarly to ferric chloride include cupric sulphate, ammonium chloride, and the chlorides of aluminium, bismuth and antimony. Modifying equation (42) for the general case where MA is the salt of a strong acid and a weak base MOH—

$$MA + H_2O \rightleftharpoons MOH + HA \quad . \quad . \quad . \quad (43)$$

or

$$\underbrace{M^+ + A'}_{\text{salt}} + H_2O \rightleftharpoons \underset{\text{weak base}}{MOH} + \underbrace{H^+ + A'}_{\text{strong acid}} \quad . \quad . \quad (44)$$

Applying the Law of Mass Action to equation (44)—

$$\frac{[MOH]\,[H^+]\,[A']}{[M^+]\,[A']\,[H_2O]} = K_H \quad . \quad . \quad . \quad . \quad (45)$$

Since

$$MOH = \frac{[M^+]\,[OH']}{K_{MOH}}$$

and omitting water since its concentration may be assumed to be constant in dilute solution, equation (45) above may be simplified to—

$$\frac{[M^+]\,[OH']\,[H^+]\,[A']}{[M^+]\,[A']\,K_{MOH}} = K_H \quad . \quad . \quad . \quad (46)$$

Therefore,

$$\frac{[OH']\,[H^+]}{K_{MOH}} = K_H \quad . \quad . \quad . \quad . \quad (47)$$

Since,

$$[OH']\,[H^+] = K_w$$

Therefore,

$$\frac{K_w}{K_{MOH}} = K_H \quad . \quad . \quad . \quad . \quad . \quad (48)$$

or, in words, the hydrolysis constant for a salt of a strong acid and a weak base is proportional to the ionic product for water and inversely proportional to the dissociation constant for the weak base involved.

By arguments similar to those leading to equation (37) it may be shown that in aqueous solution the salts of strong acids and weak bases exhibit increasing degree of hydrolysis with increasing dilution.

Salts of Weak Acids and Weak Bases. In a similar manner to that employed in the previous two cases the Law of Mass Action may be applied to the hydrolysis in aqueous solution of salts of weak acids and weak bases. The general equation for such hydrolysis may be written thus—

$$\underbrace{M^+ + A'}_{\text{salt}} + H_2O \rightleftharpoons \underset{\text{weak base}}{MOH} + \underset{\text{weak acid}}{HA} \quad . \quad . \quad . \quad (49)$$

Therefore, applying the Law of Mass Action—

$$\frac{[MOH]\,[HA]}{[M^+]\,[A']\,[H_2O]} = K \quad . \quad . \quad . \quad . \quad (50)$$

But, $[MOH] = \dfrac{[M_+]\,[OH']}{K_{MOH}}$ and $[HA] = \dfrac{[H^+]\,[A']}{K_{HA}}$

Therefore, equation (50) may be rewritten thus—

$$\frac{[M^+]\,[OH']\,[H^+]\,[A']}{[M^+]\,[A']\,[H_2O]\,K_{MOH}\,K_{HA}} = K_H \quad . \quad . \quad . \quad (51)$$

which, on ignoring water since its concentration may be assumed to be constant, may be simplified to—

$$\frac{[OH']\,[H^+]}{K_{MOH}\,K_{HA}} = K_H \quad . \quad . \quad . \quad . \quad (52)$$

Since $[OH']\,[H^+] = K_w$

therefore equation (52) may be rewritten thus—

$$\frac{K_w}{K_{MOH}\,K_{HA}} = K_H \quad . \quad . \quad . \quad . \quad (53)$$

or, in words, the hydrolysis constant for the salt of a weak acid and a weak base is proportional to the ionic product for water, and inversely proportional to the product of the dissociation constants for the weak acid and the weak base. If 1 g.mol. of the salt is dissolved in V litres of water, then at equilibrium, if h represents the degree of hydrolysis there will be h/V g.mols. of the acid HA and also of the base MOH, and $(1 - h)/V$ g.mol. of the unhydrolyzed salt and hence, since the salt is completely dissociated, of each of the ions M^+ and A'.

Therefore, applying the Law of Mass Action—

$$\frac{\left(\frac{h}{V}\right)^2}{\left(\frac{1-h}{V}\right)^2} = K_H \quad . \quad . \quad . \quad . \quad (54)$$

Therefore,
$$\frac{h^2}{(1-h)^2} = K_H \quad . \quad . \quad . \quad . \quad (55)$$

Since the quantity V has cancelled out, it follows that the degree of hydrolysis of salts of weak acids and weak bases in aqueous solution is independent of dilution. Examples of salts of weak acids and weak bases are provided by ammonium acetate and aniline acetate.

It should be noted here that the acidity or the alkalinity of aqueous solutions of such salts as those discussed above depends upon the relative strengths of the acid and the base involved. If these are of equal strength the solution, although hydrolyzed, will be neutral in reaction.

Amphoteric Electrolytes (or Ampholytes). In addition to the clear-cut acids and bases there are a number of compounds which are capable of behaving either as acids or as bases according to the conditions which obtain; such substances are known as *amphoteric electrolytes* or simply as *ampholytes*. A number of metallic hydroxides are amphoteric; examples include aluminium hydroxide, zinc hydroxide and tin hydroxide, $Sn(OH)_2$. Thus, zinc hydroxide, $Zn(OH)_2$, is capable of reacting with hydrochloric acid to form zinc chloride—

$$2HCl + Zn(OH)_2 = ZnCl_2 + 2H_2O \quad . \quad . \quad (56)$$

whilst with a caustic alkali, such as caustic soda, zinc hydroxide forms sodium zincate, thus—

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O \quad . \quad . \quad (57)$$

In zinc chloride, zinc is present as the positive zinc cation, Zn^{++}, whereas in sodium zincate, zinc is present as part of the negative zincate anion, $(ZnO_2)''$.

NEUTRALIZATION

Suppose 50 ml of a normal solution of a strong acid are titrated with a normal solution of a strong base. If when 10 ml of the base have been added to the acid the solution is diluted with water to 1 litre, there will be 40 ml of the acid remaining un-neutralized. In other words, assuming that both the acid and the base are completely dissociated, there are now 40/1000 g equivalents of the acid in the solution which occupies a volume of 1 litre; the hydrogen ion concentration in this solution is therefore 4×10^{-2}.

Since,
$$[OH'][H^+] = 1 \times 10^{-14}$$

therefore, the hydroxyl ion concentration—

$$[OH'] = \frac{1 \times 10^{-14}}{4 \times 10^{-2}}$$
$$= 2{\cdot}5 \times 10^{-13}$$

Likewise, when 20 ml of the strong base have been added to the acid the hydrogen ion concentration is 3×10^{-2}.

The hydroxyl ion concentration is therefore

$$\frac{1 \times 10^{-14}}{3 \times 10^{-2}} = 3{\cdot}3 \times 10^{-13}$$

It is thus possible to plot the *p*H value for each increment of base added. These results are shown in Table 64.

TABLE 64

*Changes in Hydrogen Ion Concentration and p*H *Value when a Strong Acid is Titrated with a Strong Base*

ml of Strong Base Added	Hydrogen Ion Concentration	*p*H Value
(50 ml of strong acid initially present)		
45·0	5×10^{-3}	2·3
49·0	1×10^{-3}	3·0
49·5	5×10^{-4}	3·3
49·9	1×10^{-4}	4·0
49·95	5×10^{-5}	4·3
50·0	1×10^{-7}	7·0
50·05	2×10^{-10}	9·7
50·1	1×10^{-10}	10·0
50·5	2×10^{-11}	10·7
51·0	1×10^{-11}	11·0
55·0	2×10^{-12}	11·7

Examination of Table 64 shows that in the region of the end point the *p*H value of the solution changes very rapidly indeed. Thus when 49·95 ml of the strong base have been added the hydrogen ion concentration is 5×10^{-5} g equivalents per litre and the *p*H value 4·3, whilst when the volume of added base is 50·05 ml the hydrogen ion concentration is 2×10^{-10} g equivalents per litre and the *p*H value 9·7. Expressed in another way, a variation of $\pm$ 0·1 ml in the region of the end point, that is, *p*H 7·0, gives rise to change in the hydrogen ion concentration of 1×10^{-4} to 1×10^{-10}, that is, a million-fold change. It will thus be obvious that solutions having hydrogen ion concentrations between *p*H 4 and *p*H 10 cannot be made up with accuracy by the simple mixing of strong acids and strong bases, owing to the very pronounced effect which small traces of acidic or alkaline impurities have upon the resulting *p*H value. The results shown in Table 64 have been plotted as a curve in Fig. 125 (Curve *I*).

Supposing that instead of a strong acid, a weak acid (e.g. acetic acid) is titrated with a strong base (e.g. sodium hydroxide), then—

$$\frac{[H^+]\,[A']}{[HA]} = K_{HA} \text{ (dissociation constant of acetic acid)} \quad . \quad (58)$$

Therefore $$[H^+] = K_{HA}\frac{[HA]}{[A']}$$

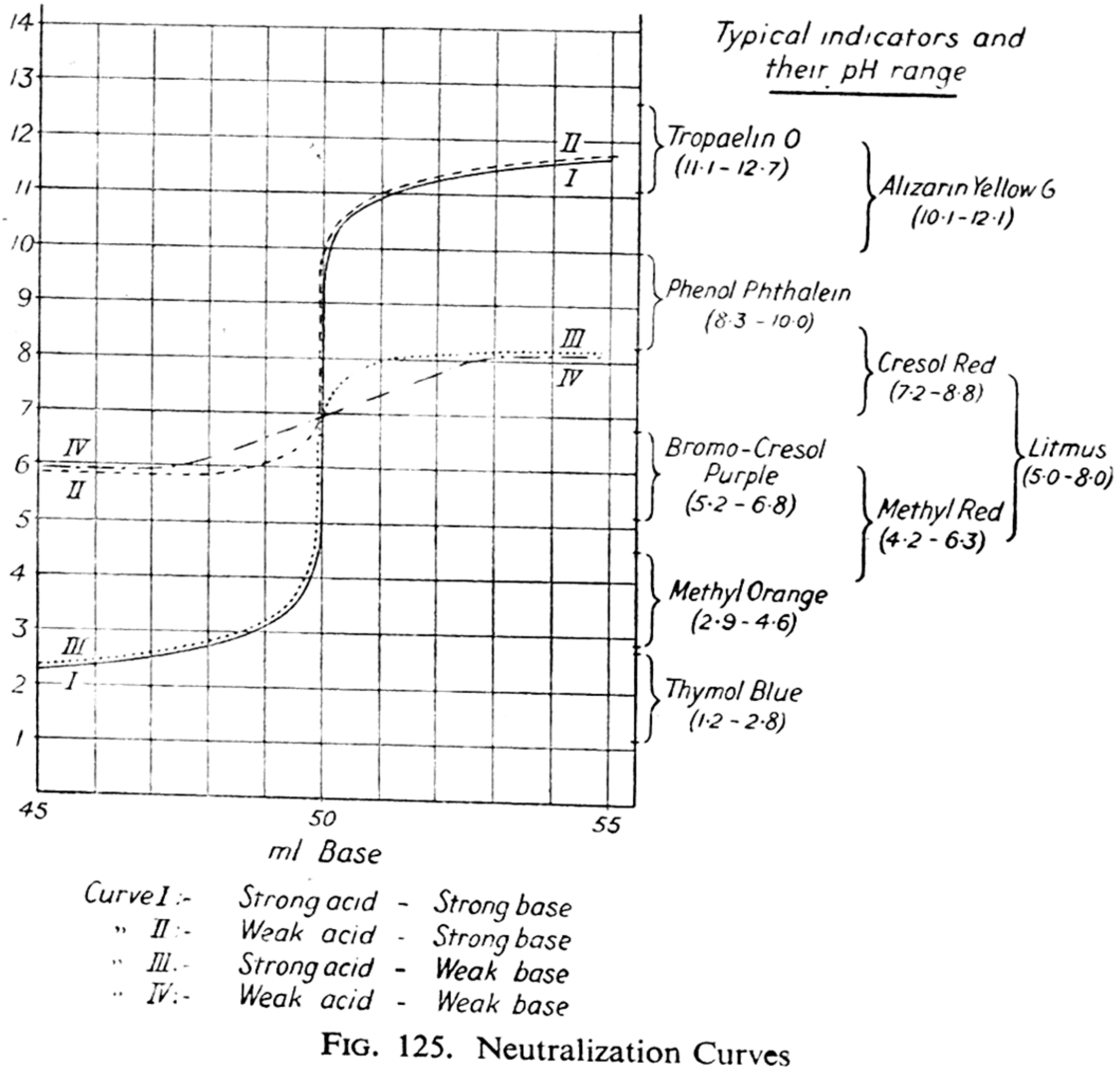


FIG. 125. Neutralization Curves

and, $$pH = \log_{10}\frac{1}{[H^+]} = \log_{10}\frac{[A']}{K_{HA}[HA]} \quad . \quad . \quad . \quad (59)$$

If the sodium acetate formed by the neutralization of the acetic acid by the sodium hydroxide is regarded as being completely dissociated then the concentration of acetate ions [A′] corresponds to the amount of base added. Also, if the acid is regarded as being very weak (i.e. very feebly

dissociated), then the concentration of acetic acid, [HA], corresponds to the whole of the residual acid.

Suppose 50 ml of N acetic acid are titrated with N sodium hydroxide. If when 10 ml of N sodium hydroxide have been added the solution is made up to one litre there will be present 40 ml N acetic acid still remaining un-neutralized; in other words, there will be 40/1000 g equivalents of acid remaining in the solution which occupies a volume of one litre; to this volume 10/1000 g equivalents of alkali have also been added.

Therefore, $[A'] = 1 \times 10^{-2}$ $[HA] = 4 \times 10^{-2}$

Therefore, introducing these values in equation (59), and taking the value of $K_{HA} = 1{\cdot}8 \times 10^{-5}$

$$pH = \log_{10} \frac{1 \times 10^{-2}}{(1{\cdot}8 \times 10^{-5}) \times (4 \times 10^{-2})}$$

$$= 4{\cdot}14$$

In this manner it is possible to calculate the variation of the *p*H of the solution accompanying each successive addition of sodium hydroxide. Some of these values are given in Table 65.

TABLE 65

Neutralization of N *Acetic Acid with* N *Sodium Hydroxide*

ml of N Sodium Hydroxide Added	*p*H
(50 ml of N acetic acid initially present)	
10·00	4·14
15·00	4·38
20·00	4·57
25·00	4·74
30·00	4·92
35·00	5·11
40·00	5·35
45·00	5·70
50·00	7·22
50·05	9·70
50·10	10·00
50·50	10·70

It should be noted from Table 65 that when the acetic acid is exactly half neutralized, that is, when 25 ml of N sodium hydroxide have been added, the concentration of acetic acid is equal to the concentration of

acetate ions, that is, [HA] = [A′], and from equation (58) it follows that the concentration of hydrogen ions is numerically equal to the dissociation constant for acetic acid. In mathematical form—

$$[H^+] = K_{HA} = 1{\cdot}8 \times 10^{-5}$$

Therefore

$$pH = 4{\cdot}74$$

Some of the results given in Table 65 are plotted in Fig. 125 (Curve *II*) from which it will be noted that prior to reaching the end point the *p*H value changes very slowly, actually, the change is least at that point in the titration when the acid is just half neutralized. This behaviour is typical of the neutralization of any weak acid by a strong base.

By a similar procedure the neutralization curve for a strong acid by a weak base may be plotted. This is shown in Fig. 125 (Curve *III*). The neutralization curve for a weak acid by a weak base is shown in Fig. 125 (Curve *IV*).

Buffer Solutions. From Fig. 125 (Curve *II*) it will be seen that the addition of small amounts of either acids or bases to solutions of a weak acid with one of its salts only gives rise to slight variations of *p*H. Thus, for example, if 0·1 ml of 0·1N hydrochloric acid is added to 10 ml of distilled water with a *p*H value of 7·0, the *p*H value of the solution will be changed to *p*H 3·0; but, if this same volume of 0·1N hydrochloric acid be added to 10 ml 0·1N ammonium acetate solution, which also has a *p*H value of 7·0, only a small change of *p*H value will occur, in fact, it will require 10 ml of 0·1N hydrochloric acid to lower the *p*H value of 0·1N ammonium acetate solution to 3·0. The reason why ammonium acetate exerts such a pronounced buffer action, and so prevents a sudden change in the *p*H value when hydrochloric acid is added may be explained as follows. The 0·1N hydrochloric acid is almost completely dissociated so that when this acid is added to water the concentration of hydrogen ions is increased accordingly; on the other hand, in aqueous solution, ammonium acetate is largely dissociated into ammonium ions and acetate ions so that the addition of hydrochloric acid (that is, the addition of hydrogen ions) leads to the hydrogen ions from the hydrochloric acid combining with the acetate ions to form molecules of feebly dissociated acetic acid; the net result is that the concentration of hydrogen ions is increased only very slightly. These changes are shown graphically in Fig. 126.

The principal salts employed as buffers include acetates, borates, citrates, phosphates and phthalates. Typical examples are—

Boric acid + borax
Citric acid + sodium citrate
Sodium phosphate + hydrochloric acid
Sodium carbonate + sodium bicarbonate
Disodium hydrogen phosphate + sodium dihydrogen phosphate

Neutralization Indicators. Neutralization indicators are examples of acidic or basic dyestuffs, that is, organic colouring matters, which exhibit a change of colour when the *p*H of the solution in which they are dissolved changes. This colour change is reversible and is usually associated with a change in constitution from a benzenoid to a quinonoid structure. The change in structure is determined by the concentration of hydrogen ions in the solution.

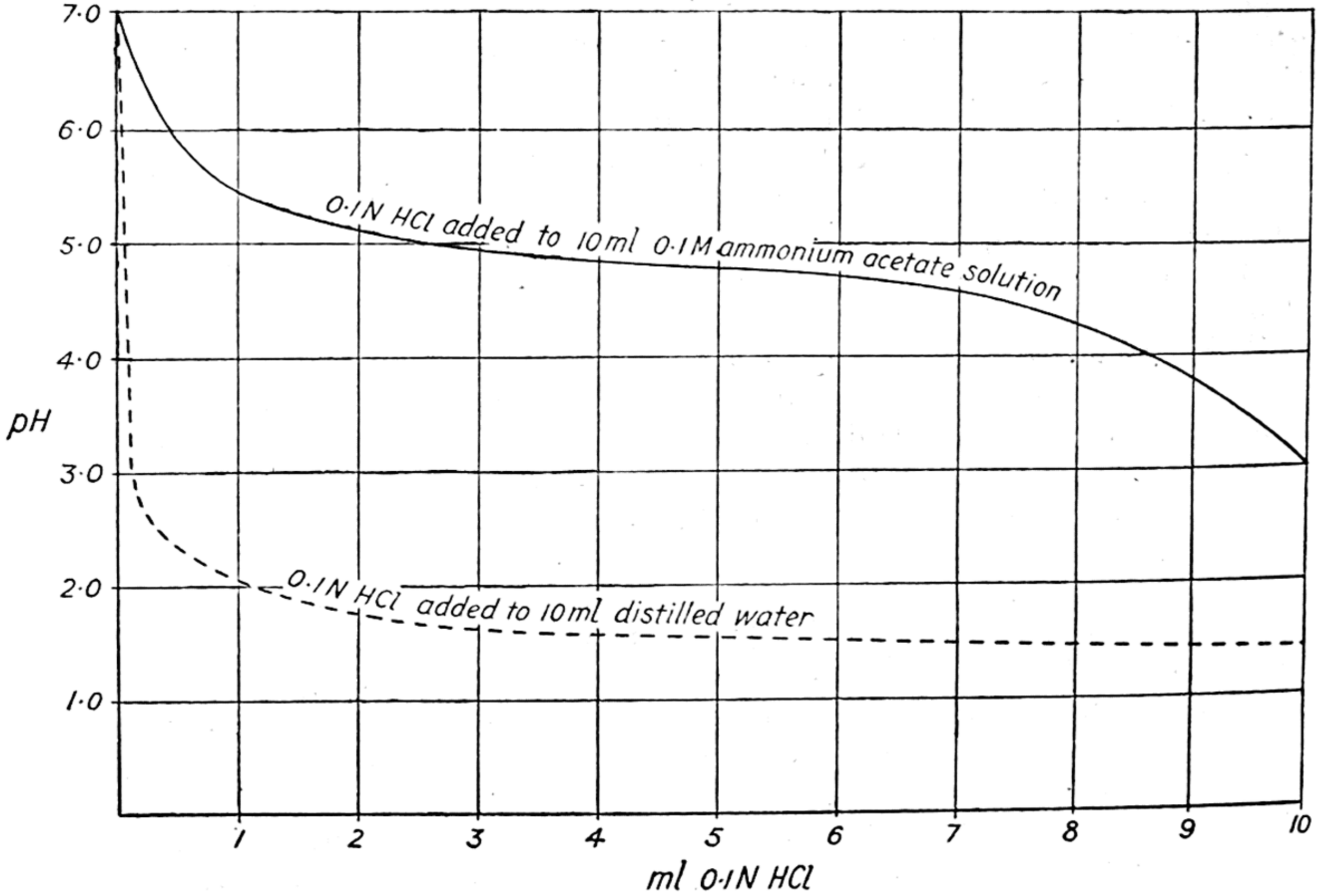


FIG. 126. Variation of *p*H when 0·1N Hydrochloric Acid is added to 10 ml of (*a*) 0·1N Ammonium Acetate, and (*b*) Distilled Water

Neutralization indicators change colour over a limited portion of the *p*H scale only; over this portion of the scale the colour change is gradual, but on either side of it there is usually no further change of colour. The colour change of such indicators takes place over ranges of approximately 1·6 *p*H.

Neutralization indicators are of two chief types, (*a*) those which are colourless in one phase and highly coloured in the other (e.g. phenol phthalein), and (*b*) those which are coloured in both phases (e.g. methyl orange).

Neutralization indicators invariably possess in one form or another the properties of either a weak base or a weak acid. If the indicator is of

one hand, and coarse suspensions on the other hand. The most important feature of the colloidal state is the co-existence of two phases, in that very finely divided particles of matter are separated from one another by a continuous medium of different composition. In general, the diameter of the particles lies between 10^{-7} and 10^{-5} cm, that is, 1 – 100 mμ (1 mμ = 0·000001 mm).

It is customary to distinguish between the *disperse phase*—the finely divided particles, and the *dispersion medium*—the medium in which the particles are distributed; the whole constituting a *dispersion system*.

Types of Dispersion System

Both the disperse phase and the dispersion medium may be solid, liquid or gaseous substances, so that the possibility exists for a variety of systems as shown in Table 68.

Colloidal systems are often termed "sols" in order to distinguish them from true solutions.

TABLE 68

Types of Colloidal System

	Dispersion Medium	Disperse Phase	Example
I	Gas	Solid	Smokes, dusts
	Gas	Liquid	Fog, mist, cloud
II	Liquid	Solid	Colloidal solution
	Liquid	Liquid	Emulsions (milk, salad cream)
	Liquid	Gas	Foams
	Stiff liquid	Solid	Ruby glass
III	Solid	Gas, liquid or solid	Many minerals

Colloidal systems in which the dispersion medium is a gas and the disperse phase a solid are often termed *aerosols*. Systems in which the dispersion medium is a liquid are referred to as *colloidal solutions*; such systems are not only very common, but they are also of considerable importance.

Sometimes the qualifying terms, *aquasol* (or *hydrosol*) and *alcosol* are employed when the dispersion media are water and alcohol respectively. Colloidal systems in which the dispersion media are organic compounds are frequently termed *organosols*.

Colloidal Systems having Liquid Dispersion Media

Systems of this type may be subdivided into two groups—

(*A*) Lyophobic (i.e. "solvent-hating") systems

(*B*) Lyophilic (i.e. "solvent-loving") systems

When water is employed as the dispersion medium, the terms, *hydrophobic* and *hydrophilic* are used to describe the systems. The chief characteristics of these two types of sols are enumerated in Table 69.

TABLE 69

Chief Characteristics of Lyophobic and Lyophilic Sols

Lyophobic Sols	Lyophilic Sols
The individual particles may readily be detected by means of the ultramicroscope	The individual particles are not readily detected by means of the ultramicroscope
The individual particles migrate in one direction only under the influence of an electric field	Under the influence of an electric field the individual particles may migrate in either direction, or alternatively, not migrate at all
The addition of small amounts of an electrolyte causes precipitation of the sol	The addition of small amounts of electrolytes has little effect upon the sol, although large amounts of electrolytes give rise to "salting out"
The viscosity of the sol is similar to that of the dispersion medium	The viscosity of the sol is much higher that that of the dispersion medium
The surface tension of the sol is similar to that of the dispersion medium	The surface tension of the sol is generally lower than that of the dispersion medium
On evaporation or cooling, lyophobic sols give solids which are not readily re-converted into sols by the simple addition of solvent Thus, lyophobic sols are often termed "irreversible sols"	On evaporation or cooling, lyophilic sols form "gels" from which the sol may again be obtained by the addition of the solvent Thus, lyophilic sols are often termed "reversible sols"
Examples of lyophobic sols. Metals, sulphur, sulphides and silver halides	*Examples of lyophilic sols.* Starches, gums, soaps and proteins

LYOPHOBIC SOLS

Brownian Movement. In a colloidal solution the individual particles move in all directions, as do the molecules in a gas, although they seldom come into actual contact with one another since they all have electrical charges of the same sign. On account of their thermal energy these particles exhibit a condition of constant movement which increases in rapidity with decreasing particle size; this is the so-called "Brownian movement." Although particles smaller than approximately $0{\cdot}2\,\mu$* cannot be observed directly by means of an ordinary microscope, this irregular movement of the colloidal particles may be demonstrated by the ability of such small particles to scatter light. For this purpose the ultramicroscope which is shown diagrammatically in Fig. 128, is employed.

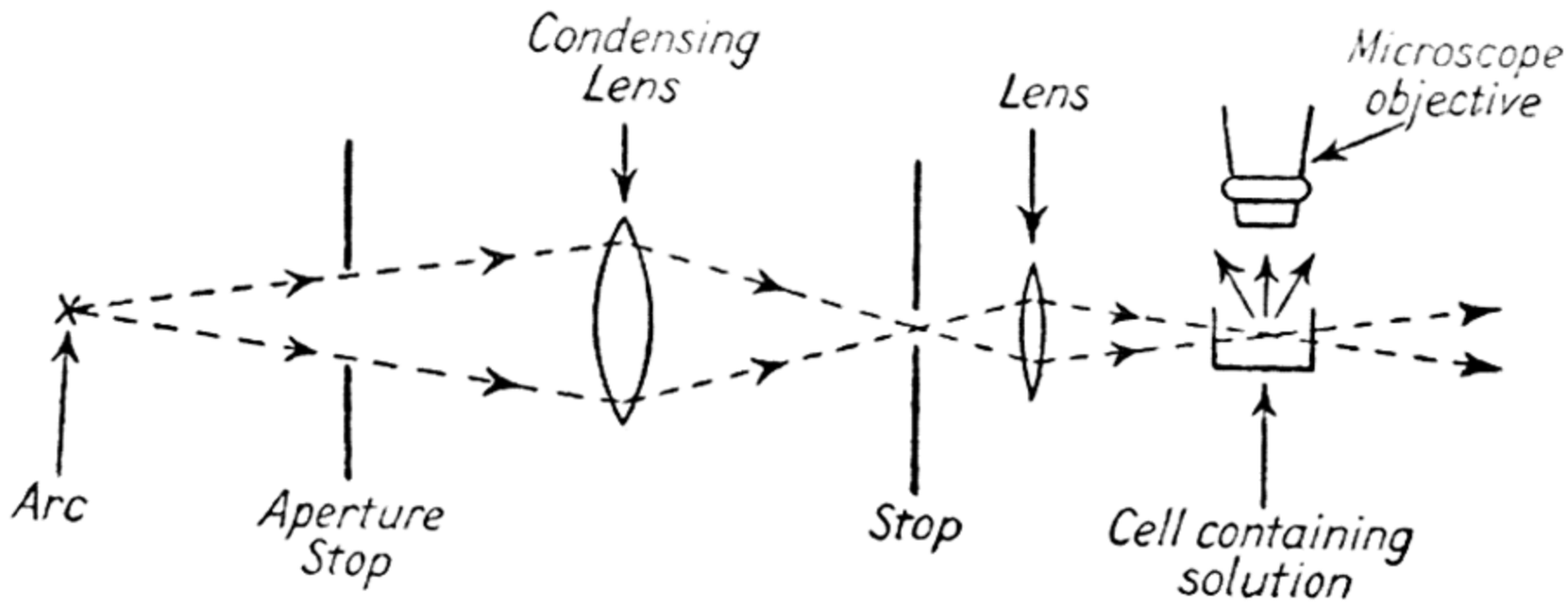


FIG. 128. Ultramicroscope

When viewed by means of the ultramicroscope each individual particle appears as a pin-point of bright light against a dark background.

Electrical Properties. If into a lyophobic sol there are immersed two electrodes to which a direct current potential is applied, the colloidal particles will migrate to one of the electrodes; this phenomenon is termed *electrophoresis* (also known as *cataphoresis*). Sols of metals, metallic sulphides, sulphur, silicic acid and acid dyestuffs are examples of negatively-charged sols which thus migrate to the anode, whilst sols of metallic oxides and hydroxides, and basic dyestuffs are positively-charged and so migrate to the cathode.

Electrophoresis is explained by the fact that at the interface between the disperse phase and the dispersion medium there exists an electrical double layer (*see* Fig. 129), the positive and negative portions of which are displaced on application of an e.m.f. to the electrodes, with the result that the particle is attracted towards that electrode having opposite polarity to itself. If between two electrodes immersed in a hydrophobic sol there is placed a porous diaphragm, the free passage of the charged colloidal particles is prevented, although water is forced towards that electrode

* $1\mu = 0{\cdot}001$ mm.

away from which the charged particles were migrating. This phenomenon, which is termed *electrosmosis*, has had important technological application in certain civil engineering projects as a means of dewatering building sites on which foundation works were in course of erection.

Precipitation by Electrolytes. The addition of an electrolyte to a lyophobic sol causes the particles to coagulate so that a precipitate is finally produced. Under ordinary conditions the electric charge resident upon the particles prevents them from coalescing, but the addition of an electrolyte gives rise to adsorption of oppositely-charged ions by the colloidal particles which thus become electrically neutral. For example, sodium chloride provides positively-charged sodium ions which, on adsorption, say by the arsenious sulphide sol, gives rise to electrically neutral particles which consequently coagulate.

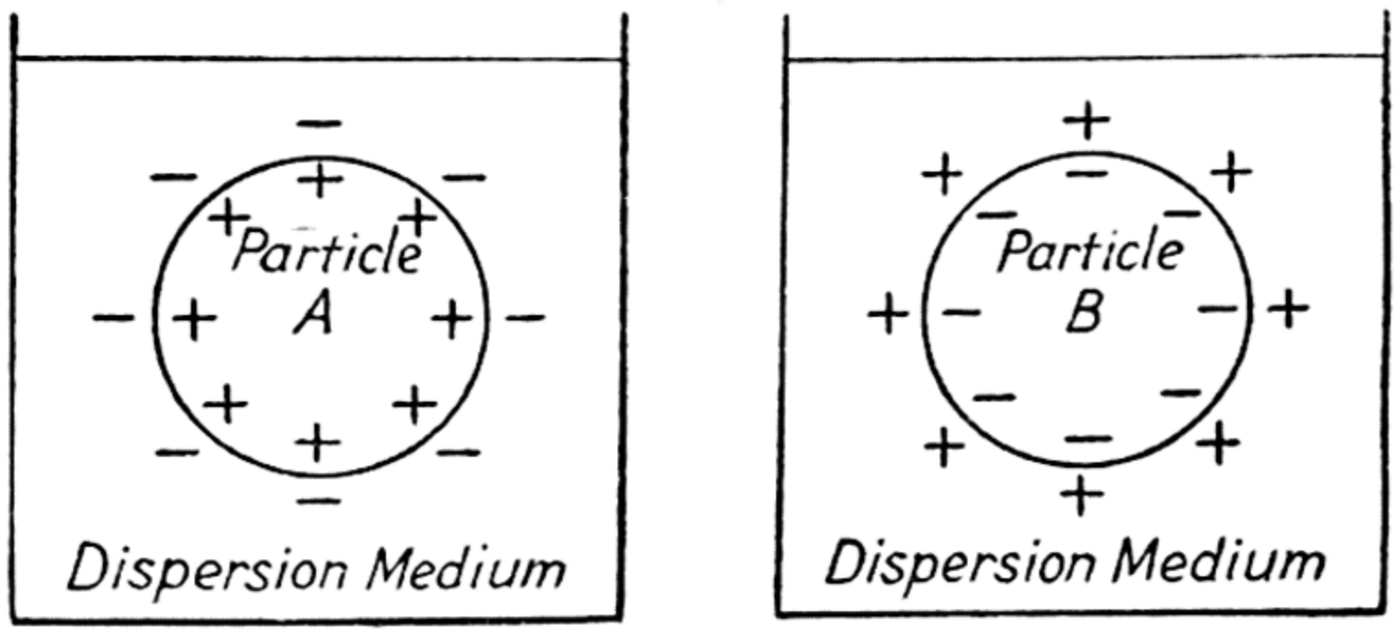


FIG. 129. Charges on Colloidal Particles (*A*) Positively Charged, (*B*) Negatively Charged

With increase in the valency of an ion of an added electrolyte, the precipitating power increases; thus, bivalent ions are roughly 100 times, and trivalent 700 times as effective as univalent ions. The strong precipitating power of the trivalent ion is illustrated by recalling that alum (which contributes the trivalent aluminium ion Al^{+++}) readily brings about the coagulation of blood, a typical colloidal substance. These facts are incorporated in the Schulze-Hardy rule which states that *the ion causing coagulation is of opposite electrical sign to that of the colloidal particle, and the coagulating power increases with increasing valency of the ion.*

Should two sols having charges of opposite electrical sign be mixed, mutual precipitation will occur; this is exemplified by the co-precipitation of the negatively-charged arsenious sulphide sol and the positively-charged ferric oxide sol when these two sols are mixed.

Adsorption Indicators. Adsorption effects similar to those described above are utilized when the so-called *adsorption indicators* are employed for determining the end-point in certain types of precipitation titrations. Adsorption indicators are chiefly derivatives of fluorescein, and to illustrate the principle underlying their application the titration of sodium chloride with silver nitrate will be taken as example. When a solution of silver

nitrate is added to a solution of sodium chloride the precipitate of silver chloride initially formed exists, partially at least, in the colloidal condition. Now, colloidal particles tend to adsorb their own ions, therefore, previous to the end-point, sodium chloride is in excess and the colloidal particles of silver chloride adsorb chloride ions to form the negatively-charged complex ion which may be represented in symbolic form as [AgCl]Cl′.

Adsorption indicators such as fluorescein and its derivatives are weak acids in which the active ion, in so far as adsorption is concerned, is the negatively-charged, red coloured anion which is incapable of adsorption by the negatively-charged complex [AgCl]Cl′. However, when the end point of this titration is passed the colloidal particles of silver chloride immediately absorb silver ions, since these ions are then in excess, so that particles of the positively-charged complex [AgCl]Ag^+ thus formed are then capable of adsorbing the red-coloured anions from the indicator. It will have been noted in the above discussion that the change in the sign of the charge on the colloidal particles does not occur until a definite excess of titrant is present, but since only a very slight excess of titrant is necessary, the end point may be determined with considerable precision. Some typical adsorption indicators and their characteristics are given in Table 70.

TABLE 70

Acidic Adsorption Indicators for Use in the Titration of Halides

Name	Colour Change	Suitable for Titration of	Condition Governing Use
Dibromo dimethyl fluorescein	Orange to pink	Chlorides	
Dichloro fluorescein . .	Yellow-green to pink	Bromides and chlorides	Slightly acid solution
Eosin	Pink to deep pink	Bromides and iodides	In neutral or acid solution
Fluorescein . . .	Green to pink	Chlorides, bromides and iodides	In neutral solution only
Rose bengal (Tetraiodo-tetrachloro fluorescein) . .	Deep pink to bluish pink	Iodides	

In addition to acid adsorption indicators such as those quoted in Table 70, there are also in use basic adsorption indicators in which the effective ion is the cation.

LYOPHILIC SOLS

Precipitation by Electrolytes. Lyophilic sols are much more stable towards small additions of precipitating agents than are lyophobic sols. In fact, it is possible to obtain lyophilic sols without electric charge when the particles do not exhibit electrophoresis, but nevertheless the sol is quite stable. Under these conditions lyophilic sols are said to be in the *iso-electric* state. This stability is thought to be due, partly at least, to hydration of the colloidal particles, the resulting hydrated "shell" protecting the "bare" particle from the coagulating effect of an added precipitating agent. The addition of large amounts of precipitating agents to lyophilic sols, however, usually results in precipitation, this effect being termed *salting out* by analogy to the precipitation of salts in true solutions by the addition of electrolytes.

Protection. The addition of a hydrophilic sol to a hydrophobic sol often stabilizes or protects the latter so that coagulation does not occur so readily on addition of a precipitating agent such as an electrolyte. This effect is known as *protection*. The protective action of lyophilic sols is expressed in terms of the *gold number*; this is defined as the least weight (in mg) of the lyophilic sol which must be added to 10 ml of a standard gold sol to prevent a colour change from red to blue on the addition of 1 ml of a 10 per cent aqueous solution of sodium chloride. Some typical values of gold numbers and their reciprocals which serve as an index to the relative protective efficiency of a lyophilic sol are given in Table 71.

TABLE 71

Gold Numbers and their Reciprocals for Typical Lyophilic Sols

Sol	Gold Number	Reciprocal of Gold Number
Gelatine . . .	0·005–0·01	200–100
Sodium caseinate .	0·01	100
Haemoglobin . .	0·03–0·07	33–14
Gum arabic . .	0·15–0·25	7–4
Sodium oleate . .	0·4–1·0	2·5–1
Gum tragacanth . .	2·0	0·5
Potato starch . .	25·0	0·04

Viscosity of Lyophilic Sols. Compared with lyophobic sols, lyophilic sols are characterized by high viscosities, these high values being probably due to the considerable degree of solvation which the latter type of sols suffer, so giving rise to the existence of very large particles.

Thixotropy. The addition of small quantities of an electrolyte to certain sols, for example gelatine sols, concentrated ferric oxide sol, and suspensions of fine clays (e.g. the bentonites), results in the formation of a pasty gel which is characterized by the ability to liquefy on shaking, but to regain its gel form on standing; this phenomenon is termed *thixotropy*.

PREPARATION OF COLLOIDAL SOLUTIONS

In the case of those substances which form lyophilic sols, simple warming of the substance with a selected dispersion medium is usually all that is necessary to attain the colloidal condition. On the other hand, for the preparation of lyophobic sols, special methods have to be employed. Since in the colloidal state the particle size of the disperse phase is intermediate between the size of solute particles in a true solution and the size of particles in an ordinary suspension, there are two general methods of approach possible in preparing lyophobic sols. They are condensation methods and dispersion methods.

Condensation Methods

In preparing lyophobic sols by condensation methods it is important to keep in mind that the substance should be produced or liberated rapidly in a dispersion medium in which it is only very slightly soluble. This was first suggested by von Weimarn (1908 onwards) who showed that *the diameter of the particles is reduced by selecting a liquid in which the precipitate is only very slightly soluble, and by effecting precipitation from very concentrated solutions*; this statement is usually known as von Weimarn's rule. Some typical examples of condensation methods are given below.

Hydrolysis. This method is useful to obtain sols of oxides or of hydroxides of weakly electropositive metals such as iron and aluminium. For example, ferric hydroxide sol is obtained by adding a small volume of concentrated ferric chloride solution to a large volume of boiling water; hydrolysis takes place and ferric hydroxide and hydrochloric acid are produced as follows.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

The hydrochloric acid and excess ferric chloride are removed by dialysis leaving the ferric hydroxide in colloidal solution. Silicic acid sol may be obtained by the hydrolysis of silicon sulphide, or of methyl or ethyl orthosilicates. Other hydroxide sols may be obtained by the hydrolysis of the nitrates of aluminium, chromium, iron and bismuth.

Double Decomposition Method. The preparation of arsenious sulphide sol provides an example of this method. When hydrogen sulphide is passed through a cold saturated aqueous solution of arsenious oxide the

bright yellow sol is produced. In a similar manner, mercuric sulphide sol may be prepared by passing hydrogen sulphide through a cold dilute aqueous solution of mercuric cyanide.

Oxidation Method. This method is exemplified by the formation of sulphur sols when aqueous solutions of hydrogen sulphide are oxidized by the oxygen of the air, by sulphur dioxide or by other oxidizing media such as nitric acid or ferric chloride which may be present in a substance undergoing qualitative analysis.

In a similar manner, selenium sols may be prepared by the oxidation of aqueous solution of hydrogen selenide.

Chemical Reduction Method. Metals are often obtained in the colloidal state by reduction of solutions of their salts by means of reducing agents. Typical reducing agents include formaldehyde, hydrazine, hydrogen and phosphorus; inorganic reducing agents are of less general application than organic reducing agents since they give rise to the precipitation of particles of greater size than those of colloidal dimensions.

Colloidal gold may be obtained by the reduction of chlorauric acid by tannic acid, formaldehyde, hydrazine, or white phosphorus dissolved in ether.

Colloidal silver is obtained by the reduction of silver nitrate solution with hydrazine. Other precious metals such as those of the platinum group may also be obtained as colloids by reduction with hydrazine. These sols appear red or brown in colour when examined by transmitted light and blue by reflected light.

Exchange of Solvent. This method is exemplified by the formation of stearic acid sol which is obtained when a hot, concentrated alcoholic solution of stearic acid is poured into water, in which stearic acid is only very slightly soluble. This is in accord with von Weimarn's rule.

Dispersion Methods

The Colloid Mill Method. In the colloid mill, two or more circular plates rotate at a high speed, each in the opposite direction to its neighbours. Into the space between the plates a suspension of the solid in the dispersion medium is slowly fed, a protective agent often being added as well. As a result of the grinding process the particle size is finally reduced to colloidal dimensions. This method is of considerable industrial importance.

Bredig's Method. In this method an electric arc is struck between electrodes of a metal immersed in a selected dispersion medium; the electrodes are of the metal which it is desired to obtain in the colloidal state. The intensity of the electric arc causes disintegration of the metal constituting the electrodes.

Peptization by Ions. Freshly precipitated substances may often be reconverted into the colloidal particles which have coagulated to form the

precipitate, by the addition of suitable reagents, usually those having one ion in common with the precipitated substance.

Freshly precipitated ferric hydroxide, obtained by the interaction of ferric chloride and ammonium hydroxide, may be *peptized* by ferric chloride. Similarly, many sulphide precipitates may be converted to the colloidal condition by passing hydrogen sulphide through an aqueous suspension of the precipitate; the hydrogen sulphide is the peptizing agent in such cases.

Washing Methods. It is well known that a precipitate tends to run through the filter paper when being washed free from electrolytes. This is due to the fact that the electrolytes were initially responsible for causing the substance to coagulate to form a precipitate and the removal of the electrolyte leaves the precipitate free to assume the colloidal condition.

PART II

SYSTEMATIC INORGANIC CHEMISTRY

By

JAMES E. GARSIDE, Ph.D., M.Sc.Tech., F.R.I.C., F.I.M.

and

R. F. PHILLIPS, M.A., B.Sc. (Oxon.), Ph.D. (Lond.), F.R.I.C.

CHAPTER 15

THE INERT GASES

Introduction and Electronic Structure. The inert gases comprise the elements, helium, neon, argon, krypton, xenon and radon. These elements form the Group 0 family of the Periodic Classification and have the following electronic structures (often referred to as "the inert-gas structures")

Helium	He	2
Neon	Ne	2 . 8
Argon	A	2 . 8 . 8
Krypton	Kr	2 . 8 . 18 . 8
Xenon	Xe	2 . 8 . 18 . 18 . 8
Radon	Rn	2 . 8 . 18 . 32 . 18 . 8

These electronic structures, which are now well established as a result of the explanation of atomic line spectra in terms of quantum numbers, were originally based (see the earlier electronic arrangement shown below) on the fact that these elements are chemically inert. Since chemical reactivity is due to the number and arrangement of the orbital electrons, it followed that the inert gases must each have a particularly stable electronic structure. In passing from one inert gas to the next through the intermediate elements of the Periodic Classification, the additional electrons, therefore, enter a new and higher electronic shell, the latter becoming complete only at the next inert gas. Thus—

Helium	He	2	*Inert*
Lithium	Li	2 . 1	*Chemically reactive*
Beryllium	Be	2 . 2	
Boron	B	2 . 3	
Carbon	C	2 . 4	
Nitrogen	N	2 . 5	
Oxygen	O	2 . 6	
Fluorine	F	2 . 7	
Neon	Ne	2 . 8	*Inert*

Extending this argument to the whole of the Periodic Table suggests that the electronic structures of the inert gases are—

Helium	2	
Neon	2 . 8	(8 elements from He to Ne)
Argon	2 . 8 . 8	(8 elements from Ne to A)
Krypton	2 . 8 . 8 . 18	(18 elements from A to Kr)
Xenon	2 . 8 . 8 . 18 . 18	(18 elements from Kr to Xe)
Radon	2 . 8 . 8 . 18 . 18 . 32	(32 elements from Xe to Rn)

This arrangement was later changed to the arrangement shown at the beginning of the present chapter as a result of a more detailed knowledge of the properties of the elements and, in particular, to two facts—

(*a*) The realization that the "transition elements" are not limited to those found in Group VIII (iron, cobalt, nickel, etc.) but form a body of some nine elements which occur approximately in the middle of each long period. Since there are three long periods, there are three groups of transition elements. These elements all show variable valency (usually two and three), form coloured salts and have catalytic properties. They result from a progressive increase in the penultimate electronic orbit, the outer orbit remaining unchanged in its incomplete state—

Transition Elements

(Only the penultimate electronic orbit increases)

Scandium	Sc	2 . 8 . 9 . 2
Titanium	Ti	2 . 8 . 10 . 2
Vanadium	V	2 . 8 . 11 . 2
Chromium	Cr	2 . 8 . 12 . 2
Manganese	Mn	2 . 8 . 13 . 2
Iron	Fe	2 . 8 . 14 . 2
Cobalt	Co	2 . 8 . 15 . 2
Nickel	Ni	2 . 8 . 16 . 2
Copper	Cu	2 . 8 . 17 . 2

Similarly, the elements from yttrium to silver in the second long period and the elements from hafnium to gold in the third long period are classed as transition elements, since they all contain incomplete outermost and penultimate electronic shells.

(*b*) The discovery of a group of elements, known as the rare-earth elements, which have almost identically the same chemical properties. This

very close similarity is due to these elements having the same electronic configuration in their outermost and penultimate shells, viz.—

Rare-earth Elements

(Only the antepenultimate electronic orbit increases)

Lanthanum	La	2 . 8 . 18 . 18 . 9 . 2
Cerium	Ce	2 . 8 . 18 . 19 . 9 . 2
.....	..	.....
Lutecium	Lu	2 . 8 . 18 . 32 . 9 . 2

Historical. The original Periodic Classification of Mendeléeff did not include a Group 0 because not only were the inert gases not known at that time but their existence was not even suspected. It is true that Cavendish in 1785 showed that the atmosphere contained small quantities of some other gases besides oxygen and nitrogen, but it was not until 1894 that Lord Rayleigh carried out his classical work which led in the same year to the isolation of the inert gas *argon* by Ramsay. No vacancies, however, occurred for this new element in Mendeléeff's classification, but the realization that argon was completely different from the other elements known at that time could only mean that it was a member of a new, as yet undiscovered, family of elements. Argon was placed between chlorine (a strongly electro-negative element) and potassium (a strongly electro-positive element), and formed a member of the new family, known as Group 0. The discovery of the other elements of this family then soon followed.

In 1894 Lord Rayleigh made a series of very accurate determinations of the density of atmospheric nitrogen, and found that in each case the density was slightly greater (0·47 per cent) than that of nitrogen obtained chemically (for example, from ammonia). This very small difference, which was too great to be due to experimental error, was soon shown to be due to the presence in atmospheric nitrogen of a previously unsuspected and unrecognized gas, argon, which was isolated by Rayleigh and Ramsay in 1894. Air purified from acidic and alkaline gases (e.g. carbon dioxide, ammonia, etc.) was passed repeatedly over heated metallic copper to remove the oxygen—

$$2\,Cu + O_2 = 2CuO$$

and then over heated magnesium to remove the nitrogen—

$$3Mg + N_2 = Mg_3N_2 \text{ (magnesium nitride)}$$

A small residue of gas remained which could not be removed by either of these reactions. It was shown to be chemically inert and was called "argon."

The isolation of other inert gases soon followed. In 1895, Ramsay isolated *helium* from the gases evolved from Cleveite, a mineral of the pitchblende (radio-active) group of minerals, and like argon, helium was found to be chemically inert. Two elements of the Group 0 family were thus known.

A systematic investigation of the gases in the air by Rayleigh and Ramsay then followed. By evaporating considerable quantities (120 tons) of liquid air, they obtained a residue from which they isolated *krypton* and *xenon*; from their argon fraction they isolated *helium* and *neon* as well as argon. It followed that "argon" as originally isolated in 1894 must have been a mixture of argon and these other inert gases.

The last member of the Group 0 family, *radon*, was discovered in 1901 by Dorn in the emanation which is formed by the radio-active element radium. Originally called "niton" by Ramsay, and also known by the name "emanation," radon occurs in several isotopic forms—radon from radium, thoron from thorium, and actinon from actinium. Of these only radon is prepared industrially.

Preparation. All the inert gases, with the exception of radon, are obtained industrially from the atmosphere. The most important source of helium, however, is the natural gas which issues from the ground in certain areas, particularly in Canada and in the U.S.A. The carbon dioxide (about 0·5 per cent by volume) is first removed from the natural gas by solution in sodium hydroxide under pressure, and the remaining gas then cooled progressively to − 185°C at a pressure of 300 lb/in.^{2} Under these conditions only the helium and a small amount of nitrogen remain unliquefied. This helium-nitrogen gas mixture is led off and subjected to further cooling to liquefy and hence separate the nitrogen. The helium is then stored under high pressure in steel cylinders for distribution.

Helium is also recovered from certain minerals, such as Monazite sand, by heating to about 1000°C. The evolved gases are freed from carbon dioxide by washing with sodium hydroxide, from carbon monoxide and hydrocarbons by passing over heated copper oxide (to form carbon dioxide and steam) followed by further washing with sodium hydroxide, from nitrogen by passing over strongly heated magnesium, and finally over heated calcium to remove any remaining gases other than helium. The presence of helium in these minerals is due to the radio-active properties of the latter which result in the very slow formation of helium. The continuous nature of this radio-activity since the beginning of time may result, however, in some 1000 litres of helium being recovered from each ton of the mineral treated.

The recovery of helium, neon, argon, krypton and xenon from air is now effected during the process of obtaining oxygen by the liquefaction—fractional distillation process described on pp. 381 to 384. The method is based, as in the case of the separation of the oxygen from nitrogen, on

the small but definite differences in the boiling points of the different gases present.

TABLE 72

Boiling Points and Proportions of Gases in the Atmosphere

Gas	B. P. (°C)	Proportion in Air (by vol)
Helium . . .	— 269	1 part in 200 000
Neon	— 246	1 part in 65 000
Nitrogen . . .	— 196	78·03 per cent
Argon	— 186	0·94 per cent
Oxygen . . .	— 183	20·99 per cent
Krypton . . .	— 153	1 part in 1 000 000
Xenon	— 107	1 part in 11 000 000

The diagram (Fig. 130) shows how the inert gases concentrate in different parts of the liquid air distillation column, as a result of the differences in their boiling points.

Helium and neon, which both have boiling points well below those of nitrogen, remain (with an appreciable proportion of nitrogen) in the residual compressed air which has not liquefied. This gas is subsequently cooled to −196°C under pressure to remove the nitrogen, and the helium and neon are then separated by the use of cooled activated charcoal which preferentially adsorbs the neon.

Argon, with a boiling point between that of nitrogen and oxygen, accumulates near the bottom of the upper column, from which point it may be withdrawn together with oxygen as the major impurity. Further fractionation in an auxiliary column, followed by chemical treatment, serves to remove the oxygen and nitrogen impurities.

Krypton and xenon, with boiling points above those of the other gases present in the air, are separated near the bottom of the lower column. Chemical treatment serves to separate the oxygen and nitrogen impurities.

The present-day demand for krypton and xenon for use in filament electric lamps is so great that special modified plants have been developed which separate only these two gases from the air.

Properties. The molecular weights of the inert gases have been determined by the relative density method (*see* p. 26), the most recent accurate measurements being those of Whytlaw-Gray using an improved form of micro-balance. The absence of chemical properties preclude determination of their atomic weights by chemical methods, but if some other method could be found for determining the numbers of atoms in the molecules of the inert gases, their atomic weights could then be determined directly from the molecular weights. The specific heat method described on p. 88

provides this information. Theory shows that the ratio of the specific heat at constant pressure to that at constant volume has the value of 1·67 for a monatomic gas, and progressively lower values approaching

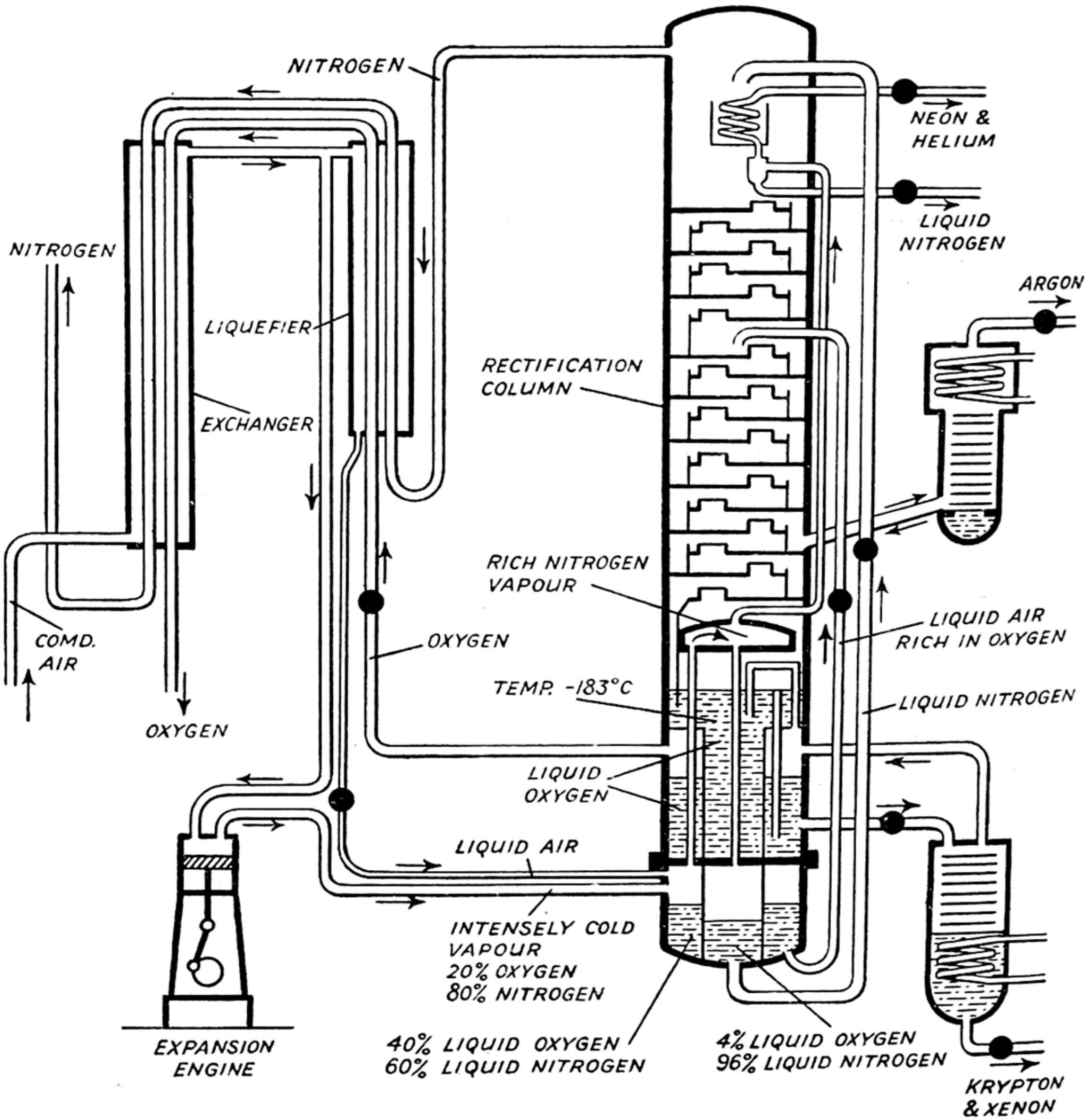


FIG. 130. Fundamental Operation of Segregating Atmospheric Gases

unity for more complicated gaseous molecules. The value of 1·67 found for the inert gases thus shows that their molecules are monatomic so that their molecular weights are also their atomic weights.

The atomic weight of argon (39·944) is slightly greater than that of potassium (39·096) the succeeding element in the Periodic Classification. On the old theory that periodicity is a function of atomic weight, this

suggests that the positions of these two elements in the Periodic Table should be reversed, with potassium coming in Group 0 and argon in Group I. The properties of these two elements, however, clearly indicate that potassium should be placed in Group I, and that argon should precede potassium in spite of its greater atomic weight. This anomaly was not explained until it was realized that atomic number and not atomic weight is the fundamental quantity which determines periodicity, and that the atomic number of argon (18) is less than that of potassium (19). The slightly higher atomic weight of argon compared with potassium is due to argon being a mixture of three isotopes (36, 38 and 40) in which the heaviest predominates whilst potassium consists mainly of the lightest of its three isotopes (39, 40 and 41).

In the following table of melting points and boiling points, it will be observed that these increase with increase in atomic weight.

TABLE 73

Boiling Points and Melting Points of Inert Gases

Inert Gas	At. Wt.	M. P.	B. P.
Helium . . .	4·002	− 272·0°C	− 268·8°C
Neon . . .	20·18	− 248·7°C	− 245·9°C
Argon . . .	39·94	− 188·0°C	− 186·0°C
Krypton . . .	83·7	− 169·0°C	− 151·7°C
Xenon . . .	131·3	− 140·0°C	− 109·0°C
Radon . . .	222·4	− 71·0°C	− 61·8°C

That the inert gases *are* chemically inert has long been accepted as a fact, but recent investigations suggest that under certain conditions some compounds may be formed. It has been seen that the efforts of Ramsay to prepare compounds of the inert gases proved unfruitful. The valency of these elements was therefore zero and they fitted conveniently into Group 0 of the Periodic Table. However, it is now recognized that the maximum numbers of electrons in the various electron shells is sometimes greater than are found in the inert gases, e.g.—

Shell	1	2	3	4	5	6
Maximum number of electrons ($2n^2$) . .	2	8	18	32	50	72
Argon . . .	2	8	8			
Krypton . . .	2	8	18	8		
Xenon . . .	2	8	18	18	8	
Radon . . .	2	8	18	32	18	8

It is thus seen that the elements argon, krypton, xenon and radon have incomplete outer shells, which might be capable of expansion (up to the limit of $2n^2$) if these elements acted as acceptors of electrons.

If the view that molecules co-ordinate by giving electrons to an acceptor as in $[Co \leftarrow (NH_3)_6]Cl_3$ be correct, then there appears no reason why similar co-ordination compounds should not occur also with the inert gases since they too should be able to accept electrons. If, however, co-ordination results initially from the attraction between a molecule with a dipole moment to a central ion, the likelihood of co-ordination occurring with the inert gases becomes less probable. Even on this view, however, there is the possibility that under suitable conditions a central ion might polarize an inert gas atom sufficiently for co-ordination to occur. Such compounds would be expected to be unstable at room temperatures, but this instability would not prevent their being recognized as compounds.

De Forcrand first found that a mixture of the inert gas with water when cooled under pressure formed crystalline hydrates. The number of molecules of water associated with each atom of inert gas was reported as 3·5 for argon, 5 for krypton, and 6 to 7 for xenon, although symmetry considerations suggest that these numbers should be six in each case, for example, $A.6H_2O$. It is probable that these unstable hydrates result from a dipole attraction in which the water molecule polarizes the inert gas atom to which it is attached to from a very weak co-ordination compound.

Booth and Willson (1935) studied the freezing-point curves of argon and boron trifluoride, and from the existence of a series of maxima they concluded that under pressures of the order of 40 atmospheres, and at temperatures in the range $-127°C$ to $-133°C$, compounds of the form $A(BF_3)_n$ exist, n having the values of 1, 2, 3, 6, 8 and 16.

Helium does not form compounds of this type, but under a sufficiently strong energy excitation, for example, in a discharge tube, one of its electrons may be promoted to a higher level and molecules of short life formed. Examples include HeH and He_2, compounds which are familiar to the spectroscopists though unobtainable in bulk. Similarly, Manley in 1927 found that when helium under low pressure is contained in a tube over mercury, oscillation of the latter sets up a glow discharge which is accompanied by a decrease in pressure. Very careful experiments showed the formation of a gaseous mercury helide, probably $HgHe_2$. Boomer in 1925 found that a glowing tungsten filament in helium in a discharge tube gave a solid black deposit which could be collected and weighed. The amount of helium so combined was determined from the decrease in pressure, and indicated the black deposit to be a helide of tungsten with the formula WHe_2. Damianovitch found that the use of platinum electrodes in a helium discharge tube produced a solid platinum helide.

Clathrate Compounds. H. M. Powell of Oxford has recently described the preparation and properties of certain organic compounds which contain inert gas atoms held in the solid molecular lattice. The inert gases are absorbed during crystallization of the organic compound and can only be released from their pockets in the solid crystals by melting the latter.

Uses. The increasing industrial importance of the inert gases in recent years may seem remarkable in view of their inertness and difficult availability. This increasing importance, however, is due to this lack of chemical reactivity and also to their possession of some very desirable electrical properties, both of which have led to their use in gas-filled filament lamps, in gas-conductor discharge tubes, and in the more recently developed fluorescent tubes.

Argon has now largely replaced nitrogen in gas-filled incandescent filament lamps, with considerable increase in efficiency. In some types of lamp the argon is replaced by krypton and xenon, the efficiency being further increased by one-third as a result.

TABLE 74

Gases and Types of Glass employed for Discharge Lamps

Colour	Gas	Pressure (mm)	Glass	Mercury
Deep red	Neon	10–18	Soft red	None
Red	Neon	10–18	Clear	None
Yellow	Helium	3–4	Amber	None
Light green	Argon + Neon	10–20	Green	Present
Dark green	Argon + Neon	10–20	Amber	Present
Light blue	Argon + Neon	10–20	Clear	Present
Dark blue	Argon + Neon	10–20	Purple	Present
White	Helium	3–4	Clear	None

The gas-conductor discharge tube consists of a glass tube with electrodes sealed in at each end and filled under very low pressure with various inert gases, such as neon, together sometimes with a little mercury. When a potential of the order of 5000 to 15 000 volts is applied, the inert gases develop high electrical conductivity and glow with an intense light the colour of which is determined by the composition of the gas in the tube. The current consumed is of the order of 15 to 50 milliamperes, that is, much less than with the normal filament type of lamp. Addition of a trace of an organic compound produces the so-called ripple effect.

The more recent and increasingly popular fluorescent tubes consist of

inert-gas filled tubes which are provided with a coating of a fluorescent material on the inside of the glass. This material absorbs the invisible and ultraviolet radiation emitted by the inert gas and emits instead a colour which is characteristic of the nature of the material. This light supplements the visible radiation emitted at the same time by the inert gas. The following table lists some of the more important fluorescent materials in use—

TABLE 75

Fluorescent Materials

Material	Colour Emitted
Calcium tungstate . . .	Blue
Magnesium tungstate . .	Blue-white
Zinc silicate	Green
Zinc beryllium silicate . .	Yellow-white
Cadmium silicate . . .	Yellow-pink
Cadmium borate . . .	Pink

Helium has other uses in addition to those discussed above. It is used instead of the very inflammable hydrogen in lighter-than-air craft, such as air-ships, because it is non-inflammable and has almost as great a lifting power (92·5 per cent of that of hydrogen). It is also used in admixture with oxygen to provide an "artificial-air" suitable for tunnel-workers and deep-sea divers, helium being much less soluble in the blood than is nitrogen, and this substitution tends to prevent the formation of bubbles in the blood, known as *caisson disease*, when the pressure is released.

CHAPTER 16

HYDROGEN

Occurrence. Only very small amounts of hydrogen gas occur in the atmosphere, a fact which might be anticipated from the unique position of hydrogen as both the lightest gas and lightest element. Spectroscopic observations, however, indicate the presence of the gas in certain stars and celestial bodies, and the sun's chromosphere appears very largely to be

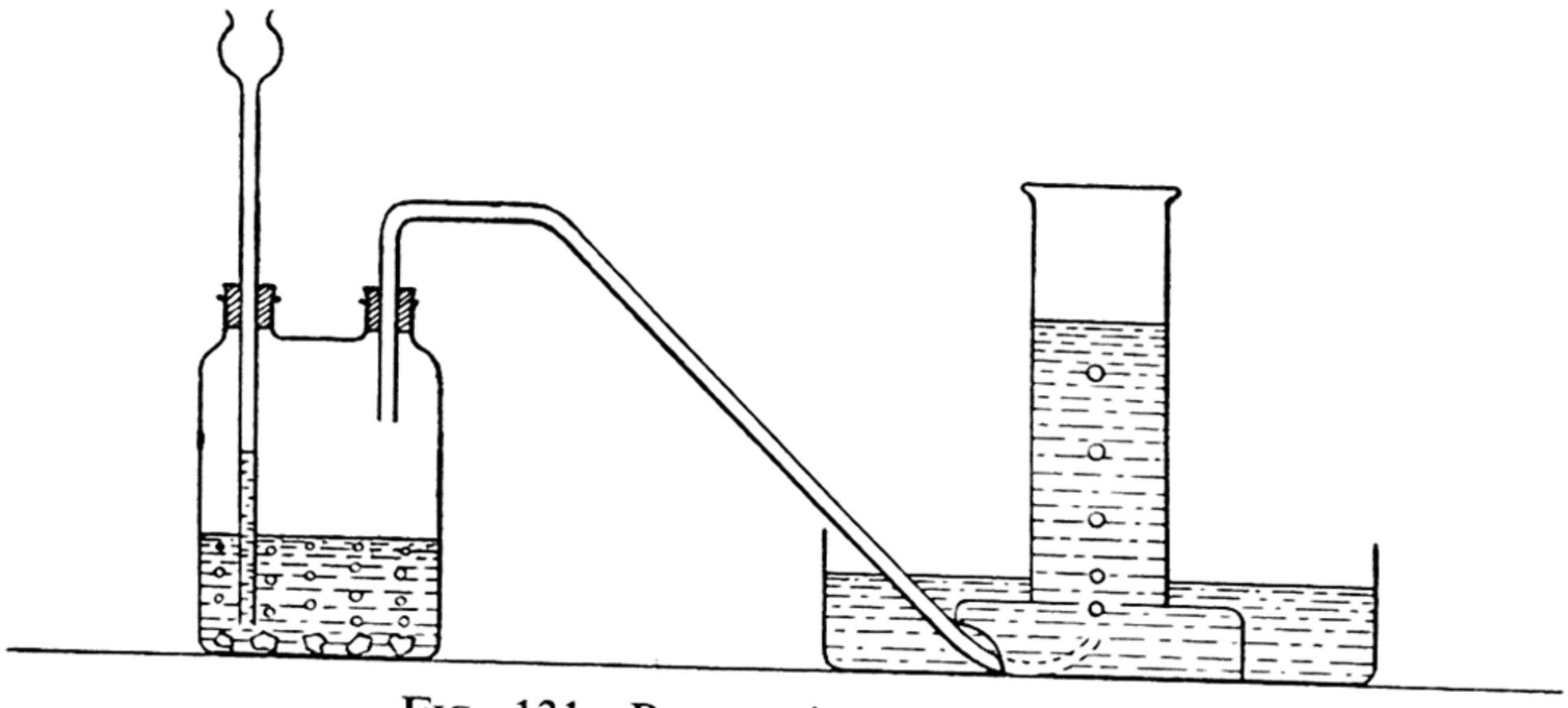


FIG. 131. Preparation of Hydrogen

made up of huge flames of burning hydrogen. In the combined state, however, hydrogen ranks as one of the more abundant elements. Water, petroleum deposits, mineral oils, organic matter such as wood, coal, fats, and so on, all reveal the abundant and wide-spread distribution of hydrogen in nature.

Preparation. Laboratory and commercial methods for preparing hydrogen all involve liberation of the combined hydrogen present in such compounds as water, the mineral acids and the alkalis. Laboratory methods, however, are not always suitable as commercial processes, and conversely the methods of the latter are not always convenient in the narrow confines and limited scope of the laboratory. This distinction between laboratory and commercial methods of preparing gases makes desirable a separate treatment, although the methods are basically the same.

Laboratory Preparation. The four methods to be discussed are—

(*a*) Action of metals on acids; (*b*) action of metals on water or steam; (*c*) action of metals on the alkalis; and (*d*) electrolytic methods.

Action of Metals on Acids

This is the usual laboratory method. The metals commonly used include granulated zinc, magnesium ribbon, or iron filings, and the acids hydrochloric or sulphuric. The diagram (Fig. 131) shows the form of apparatus which may be used to liberate and collect the gas. The zinc or other metal is first placed in the Woulfe bottle, and the dilute acid then added via the thistle funnel. The hydrogen is collected over water in the pneumatic

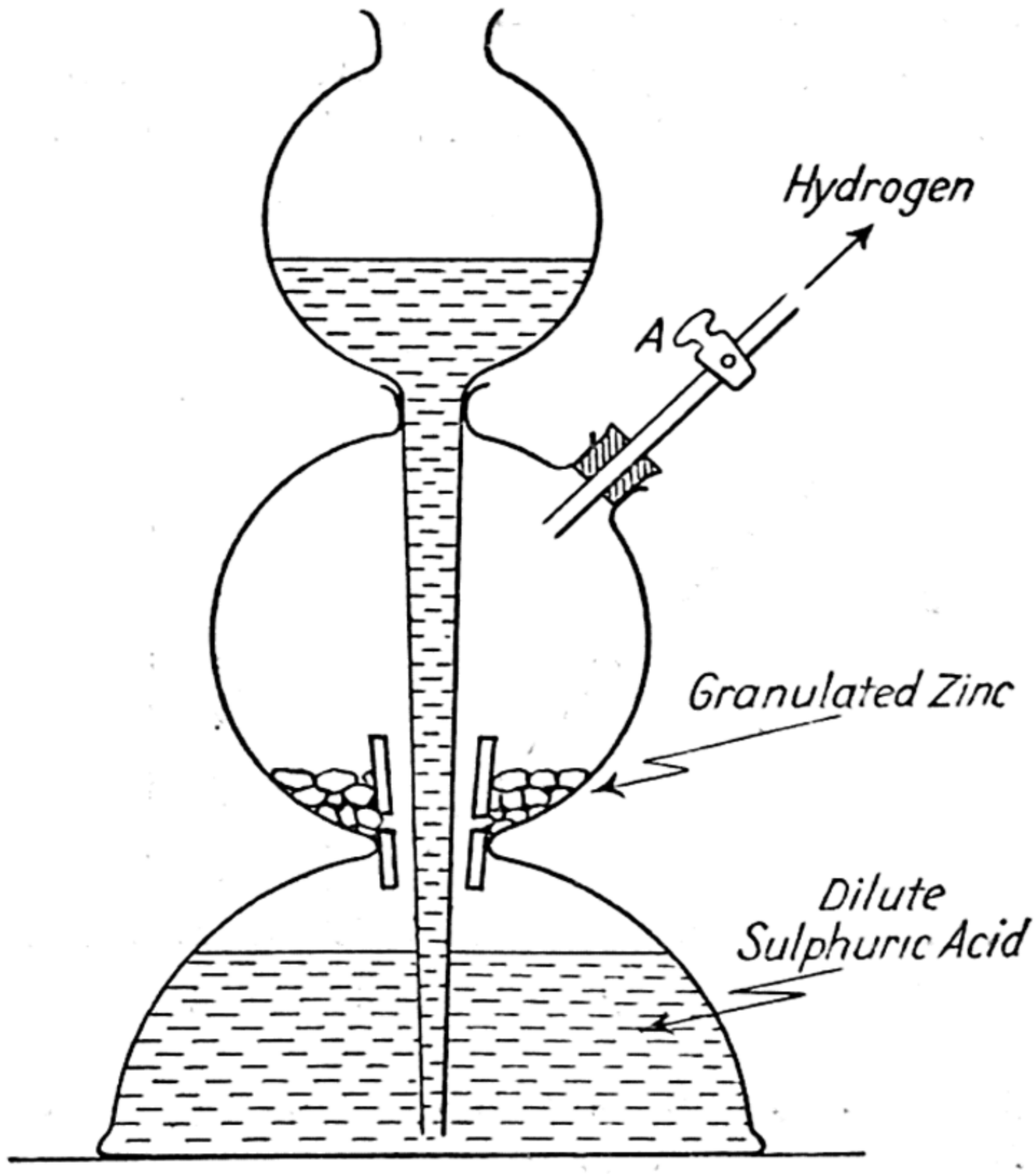


FIG. 132. Kipp's Apparatus

trough. In the case of zinc and sulphuric acid, the equation for the reaction is—

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

The reaction may also be carried out in a Kipp's apparatus if an intermittent and plentiful supply of the gas is required. One form of this apparatus is shown in Fig. 132. The granulated zinc is placed in the middle bulb and dilute acid poured into the top container. When the tap *A* is opened, the acid enters the middle bulb and reacts with the zinc to liberate hydrogen. When the tap *A* is closed, the hydrogen which continues to be generated in the middle bulb eventually depresses the level of the acid below the zinc and the reaction ceases.

The impurities present in the hydrogen prepared by this method

include arsine, AsH_3 (from arsenic impurities present in the zinc), sulphuretted hydrogen, H_2S, and sulphur dioxide, SO_2 (due to reduction of the sulphuric acid by *nascent* hydrogen), together with some hydrocarbons (from the action of hydrogen on compounds and elemental carbon present). The arsine and sulphuretted hydrogen may be removed by bubbling the hydrogen through a solution of silver nitrate, the sulphur dioxide via a solution of sodium or potassium hydroxide, and finally the hydrocarbons via a strong solution of potassium permanganate. When, however, pure hydrogen is required it is usual to prepare it by the electrolytic method described below.

Not all the metals, nor all the acids, react with equal facility to liberate hydrogen. Two factors have to be considered. These are (*a*) the chemical reactivity of the metal, and (*b*) the strength and concentration (not the same thing) of the acid. The reaction is essentially an electrolytic one involving the discharge of hydrogen ions at a metal electrode. The greater the electrode potential developed by a particular metal in a solution, the more easily will the reaction occur. For a full discussion of electrode potentials, *see* p. 267. It will be sufficient here to add that the relatively non-reactive "coinage" metals and copper have an electrode potential which is less than that for the hydrogen electrode, so that these metals cannot discharge hydrogen ions, and so do not liberate hydrogen on treatment either with water or with acids. The metals above hydrogen in the electropotential series of the metals are potentially able to do so, but the ability increases with ascent of the series.

Considering next the second factor, namely the acid, clearly the strong acids, since they produce more hydrogen ions than the weak acids (due to their greater degree of ionization), will be the more reactive. The "strong" hydrochloric acid will thus be much more effective than the feebly ionized acetic acid (vinegar). The concentration of the acid, that is, whether for example dilute or concentrated, must also affect the supply of hydrogen ions, and in general the more concentrated the acid, the more readily will hydrogen be liberated on adding the metal.

At ordinary temperatures, therefore, a reasonably rapid evolution of hydrogen will result from the reaction of—

(i) sodium or potassium with water; (ii) magnesium ribbon and very dilute hydrochloric or sulphuric acid; (iii) granulated zinc or iron filings and bench (2N) dilute hydrochloric or sulphuric acid; but (iv) tin and lead require the concentrated acids and heat.

The electrolytic nature of the reaction is further emphasized by the reluctance of *pure* zinc to react with acids. If however a drop or two of a copper sulphate solution be added, small amounts of metallic copper are deposited on the zinc by the reaction—

$$Zn + CuSO_4 = ZnSO_4 + Cu \downarrow$$

and the resulting zinc-copper couple then reacts vigorously with the acid. In this case the reaction is virtually a simple cell reaction in which the two electrodes are in contact (*see* Fig. 133).

No mention has so far been made of nitric acid, and this omission until now is due to the fact that in addition to being an acid, nitric acid is also a very good oxidizing agent. Any hydrogen liberated apparently reduces the acid so that instead of hydrogen being liberated, various oxides of nitrogen (brown gases) are evolved. If, however, the nitric acid be very dilute and a reactive metal such as magnesium be used, some hydrogen escapes and may be collected.

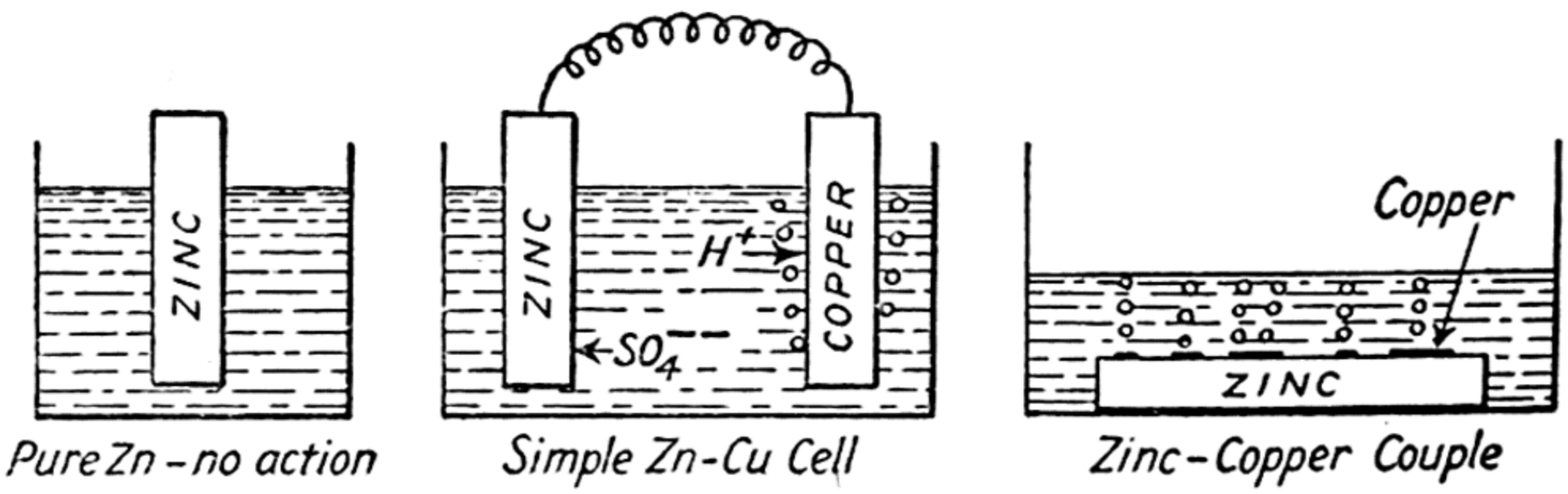


FIG. 133. Electrochemical Corrosion of a Metal

Action of Metals on Water

A detailed discussion of the reaction of the metals with water or steam is given in the properties of water (*see* p. 408). These reactions may be briefly summarized here, as follows—

(i) Very reactive metals, such as potassium and sodium, react immediately with water at ordinary temperatures to liberate hydrogen and form the corresponding hydroxides—

$$2Na + 2H_2O = 2NaOH + H_2\uparrow$$

(ii) The less reactive metals, such as magnesium and zinc, require more vigorous conditions and will burn when heated strongly in steam, in this case to form the oxide of the metal—

$$Mg + H_2O = MgO + H_2\uparrow$$

(iii) Iron and tin react without burning when heated strongly in steam, the iron reaction being the basis of a commercial method for preparing relatively pure hydrogen—

$$3Fe + 4H_2O = \underset{\text{(ferroso-ferric oxide)}}{Fe_3O_4} + 4H_2\uparrow$$

Copper and the baser metals do not liberate hydrogen from water under any conditions.

The reaction with water probably follows the electrolytic mechanism

discussed in connexion with the reaction of the metals with acids, but the reaction with steam in which the oxide of the metal is formed is presumably one of direct oxidation.

Action of Metals on Alkalis

Those metals, such as aluminium and zinc, whose oxides are amphoteric, may react with the alkalis on heating to liberate hydrogen. Thus—

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2 \uparrow$$
$$Zn + 2NaOH = Na_2ZnO_2 + H_2 \uparrow$$

In view of the discussion on the preceding two methods, the student will appreciate that this reaction is compounded of two consecutive reactions—

(i) Action of the metal on water to form an insoluble coating of the oxide or hydroxide which prevents further action by the metal—

$$Zn + 2H_2O = Zn(OH)_2 \downarrow + H_2 \uparrow$$

followed by—

(ii) Solution in the hot alkali of the oxide or hydroxide, due to its amphoteric properties.

$$Zn(OH)_2 + 2NaOH = \underset{\text{sodium zincate}}{Na_2ZnO_2} + 2H_2O$$

In the case of the aluminium, the consecutive reactions are—

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2 \uparrow$$
$$Al(OH)_3 + NaOH = \underset{\text{sodium aluminate}}{NaAlO_2} + 2H_2O$$

In each case, the continuous removal of the insoluble hydroxide coating by solution in the alkali will expose fresh surface of the metal so that the reaction occurs continuously.

Electrolytic Methods

Very pure hydrogen is usually prepared in the laboratory by the electrolysis of a warm solution of barium hydroxide, $Ba(OH)_2$, using pure nickel electrodes. Hydrogen is evolved at the cathode (negative electrode).

The older explanation for this liberation of hydrogen assumed the formation of metallic barium at the cathode by the reactions—

$Ba(OH)_2$ ionization: $Ba(OH)_2 \rightarrow Ba^{++} + 2(OH)^-$

Discharge of Ba^{++} ions at the cathode: $Ba^{++} + 2e \rightarrow Ba$

The metallic barium was then considered to react with the water present to reform barium hydroxide and liberate hydrogen—

$$Ba + 2H_2O = Ba(OH)_2 + H_2$$

It is now known that the hydrogen is formed directly by the neutralization (i.e. discharge) of hydrogen ions at the cathode. The solution of barium hydroxide contains, in addition to Ba^{++} and $(OH)^-$ ions produced by ionization of the barium hydroxide, H^+ and $(OH)^-$ ions produced by ionization of the water—

$$Ba(OH)_2 \rightleftharpoons Ba^{++} + 2(OH)^-$$
$$H_2O \rightleftharpoons H^+ + (OH)^-$$

Since H^+ ions have a lower discharge potential than Ba^{++} ions, the H^+ ions are preferentially discharged at the cathode and no metallic barium is produced. The function of the barium hydroxide, a strong electrolyte, is to increase the conductivity of the water. Although the concentration of H^+ ions in the solution is extremely small, the removal of hydrogen ions at the cathode upsets the ionization equilibrium and more water ionizes. The concentration of H^+ ions in the solution is thus maintained at a constant value throughout the electrolysis. At the anode, oxygen is liberated by the discharge of hydroxyl ions—

$$(OH)^- \rightarrow (OH) + e$$
$$4(OH) \rightarrow 2H_2O + O_2$$

The hydrogen which collects in the cathode chamber is first passed over hot platinum gauze when the following catalytic reaction (*see* p. 219) removes the small oxygen impurity carried away from the $Ba(OH)_2$ solution by the hydrogen—

$$2H_2 + O_2 = 2H_2O$$

The gas is then passed over phosphorus pentoxide to dry it and finally adsorbed in freshly activated palladium metal, from which it may subsequently be regenerated by heating. A modification of the palladium adsorption technique consists in allowing the hydrogen to diffuse through an electrically heated palladium thimble. This method of purifying hydrogen may also be applied to hydrogen prepared by the other methods, so long as any arsenic and sulphur compounds which would tend to poison the platinum catalyst are first removed.

Commercial Processes. The principal commercial processes for preparing hydrogen are—

(*a*) Electrolytic methods; (*b*) the iron-steam or Lane process; (*c*) the water-gas or Bosch process; (*d*) the thermal "cracking" of hydrocarbon gases; (*e*) the action of steam on hydrocarbon gases; (*f*) from ammonia; and (*g*) from coke-oven gases.

Electrolytic Methods

Where electrical power is cheap, and only a moderate amount of hydrogen is required, the best method appears to be the electrolysis of a dilute

aqueous solution of sodium hydroxide using usually an iron cathode and a nickel-plated iron anode. The reactions involved are those discussed above. A considerable amount of hydrogen however, is also obtained as a by-product of the electrolysis of sodium chloride solution in the manufacture of sodium hydroxide (*see* p. 428).

The Lane or Iron-Steam Process

Hydrogen of about 98 per cent purity is produced by passing excess of steam over a bed of spongy or "reduced" iron, heated externally to about 650°C. The steam reacts with the iron to form black magnetic oxide, Fe_3O_4, and the liberated hydrogen is carried away by the excess of steam.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2\uparrow$$

The "$\rightleftharpoons$" sign indicates that the reaction is a reversible one. By passing excess of hydrogen over the heated Fe_3O_4, the reaction occurs in the reverse direction and results in the formation of metallic iron and steam, together with the excess of hydrogen. This fact is utilized to convert the Fe_3O_4 back to metallic iron. For this purpose, water gas, produced by the action of steam on white hot coke, is used as the source of hydrogen—

$$H_2O + C \underset{\text{coke}}{=} CO + H_2$$

In practice, the two processes are carried out alternately. The steam is passed over the iron bed for some ten minutes and the resulting hydrogen collected; the steam is then shut off and water gas ($CO + H_2$) is then passed over for about twenty minutes. The waste water-gas issuing from the reaction chambers is then allowed to burn around the retorts to maintain the temperature of the iron at 650°C.

The Water-Gas or Bosch Process

Water gas (*see* p. 229) is mixed with excess of steam and passed at about 450°–500°C over a catalyst of the iron oxide type activated by chromic oxide.

$$H_2O + \underbrace{CO + H_2}_{\text{water gas}} \rightleftharpoons CO_2 + 2H_2 + 10\,000 \text{ cal.}$$
$$\text{steam}$$

The reaction is reversible and exothermic, and so is carried out in the presence of a catalyst. The excess of steam is necessary to increase the equilibrium conversion of the carbon monoxide to carbon dioxide and hydrogen. The hydrogen so produced contains carbon dioxide (mainly) and some carbon monoxide. The carbon dioxide is removed by washing with water under 25–50 atmospheres pressure (CO_2 gas is very soluble in water under pressure), and the carbon monoxide then removed by washing at 200 atmospheres pressure with an ammoniacal solution of a cuprous salt (e.g. Cu_2Cl_2) or with a hot solution of sodium formate.

The Thermal Process

Hydrogen is now produced very cheaply from the natural gases (methane, ethane, etc.) issuing from oil wells. These are decomposed by passing over chequer-brickwork heated to a temperature of about 1200°C. Carbon black is a very valuable by-product.

$$CH_4 = C + 2H_2; \quad C_2H_6 = 2C + 3H_2$$

Hydrogen is also prepared from natural gases, (which have been purified from sulphur compounds), by reaction with steam in presence of alumina as catalyst—

$$CH_4 + H_2O = CO + 3H_2$$

The yield of hydrogen is increased by admixture with more steam and passing over a suitable iron catalyst at 1100°C, or over activated nickel at 800°C—

$$CO + H_2O = CO_2 + H_2$$

Partial Liquefaction of Coke-oven Gas

Considerable quantities of hydrogen are nowadays recovered from the gases issuing from coke-ovens (*see* p. 591). Liquid nitrogen, produced in large quantities as a more or less waste product in the industrial process of manufacturing oxygen by the fractional distillation of liquid air, is used to liquefy and hence separate the less volatile gases (hydrocarbons, carbon dioxide, etc.) present in coke-oven gas. Any remaining carbon dioxide is removed by washing with ammonia solution, and the residual gas, mainly hydrogen and nitrogen, is mostly used in the manufacture of ammonia by the Haber Process.

From Ammonia

When ammonia gas is heated to about 850°C and passed over an activated catalyst, it decomposes to produce a gas composed of three volumes of hydrogen and one volume of nitrogen.

$$2NH_3 = 3H_2 + N_2$$

Where a supply of liquid ammonia in cylinders is economically available, this method is useful in providing a non-oxidizing nitrogen-rich gas for the heat-treatment of metals.

Physical Properties of Hydrogen. Colourless, odourless and tasteless, hydrogen is almost insoluble in water (2 vols in 100 vols water at 0°C); it is the lightest gas known, is very difficult to liquefy and solidify, and although not poisonous will not support life. The three properties, solubility, ease of liquefaction and action on litmus (i.e. acidic or basic), are really related properties. Non-reactive gases in general show only feeble solubility in water, little if any reaction towards litmus and are difficult

to liquefy. Other gases, such as hydrogen chloride and ammonia, which are very soluble in water, are also either strongly acidic or alkaline towards litmus, and are easily liquefied and solidified. Gases having intermediate solubility, for example, sulphur dioxide and carbon dioxide, are feebly acidic or basic, and moderately easy to liquefy.

An interesting physical property of hydrogen is its enormous solubility in palladium metal, especially when the latter has been pre-activated by heating. Certain other metals show the same property to a lesser degree. The palladium adsorption, or, as it is usually called, occlusion, of hydrogen finds practical application in the preparation of pure hydrogen for research purposes. At ordinary temperatures, palladium may occlude as much as 1000 times its own volume of hydrogen. On subsequent heating, the hydrogen is released. Morley used this occlusion in palladium to collect and weigh hydrogen in his classical determination of the combining weights of hydrogen and oxygen, (*see* p. 402).

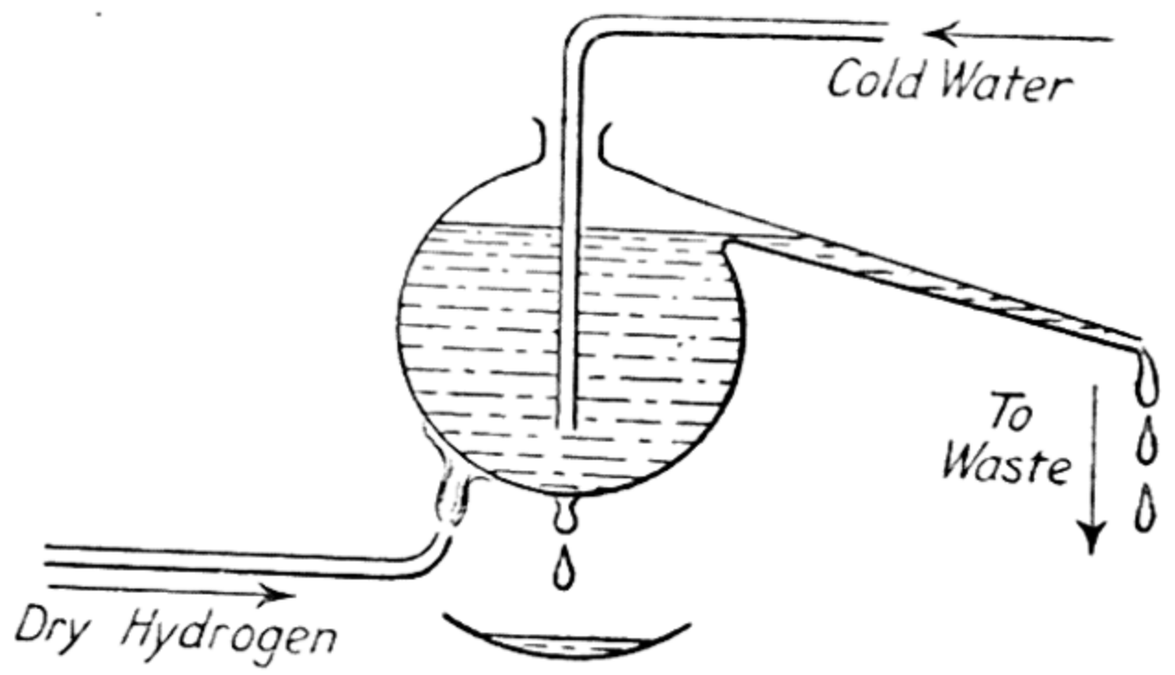


FIG. 134. Burning Dry Hydrogen in Air to Form Water

Chemical Properties. At ordinary temperatures, hydrogen gas is quite stable. It exists as diatomic molecules, H_2, in which each hydrogen atom has acquired the helium (inert-gas) electronic structure by sharing one of its electrons with the other, and so forming a covalent link, i.e. hydrogen atom, $H\times$; hydrogen molecule, $H^{\times}_{\times}H$ or H—H. The reactivity of hydrogen at higher temperatures is attributed to a small tendency of the molecules to dissociate into reactive, electron-deficient, free hydrogen atoms (*see* p. 373).

Hydrogen burns in air or oxygen with a scarcely visible blue flame to form water. If the reaction is carried out using the apparatus as shown in the diagram (Fig. 134) the water may be condensed and collected.

$$2H_2 + O_2 = 2H_2O$$

If, instead of allowing the hydrogen to burn in this way, it is mixed with air or oxygen and then ignited or sparked, a violent explosion may result. The familiar test in which the open end of a test-tube containing hydrogen is brought to a bunsen flame to produce a "pop," is a very mild example of this explosive power. Consequently, whenever hydrogen (methane, ethylene, acetylene also) is prepared in the laboratory, it is essential to allow the hydrogen to pass freely for some time in order to displace any air present, before applying a light to the hydrogen at the delivery end of the apparatus. Failure to observe this necessary precaution may cause a

serious explosion. This reaction between hydrogen and oxygen will however take place quietly at ordinary temperatures if the mixed gases are passed over a very finely divided platinum (or palladium) catalyst, a reaction which is used as described earlier to remove oxygen impurity from hydrogen.

Hydrogen will also combine under certain conditions with most non-metals and with some metals. Thus chlorine and hydrogen will combine when exposed to sunlight, and also by burning one gas in the other.

$$H_2 + Cl_2 = 2HCl$$

hydrogen chloride gas

The reaction in sunlight results from the photochemical dissociation of a very small proportion of the chlorine molecules to produce reactive chlorine atoms—

$$Cl_2 + h\nu = 2(Cl)$$

light energy

The very reactive chlorine atoms react immediately with hydrogen

$$H_2 + (Cl) = HCl + (H)$$

to form hydrogen chloride and a hydrogen atom, and the latter, in its turn, reacts with a chlorine molecule to liberate another chlorine atom and so on.

$$(H) + Cl_2 = HCl + (Cl);\ \ (Cl) + H_2 = HCl + (H);\ \text{etc.}$$

Such a reaction is known as a *chain reaction*, and it is this type of reaction which is responsible for many gaseous explosions. The energy required for the small initial dissociation of one of the reacting molecules into free atoms may be photochemical (action of light), or thermal (flame or electric spark). Examples in which chain reactions occur include the explosion of methane-air mixtures in coal mines, and the explosion of petrol vapour—air mixtures in the automobile or ignition engine.

Nitrogen and hydrogen require a high temperature and pressure and the presence of a catalyst before any appreciable reaction occurs to form ammonia—

$$N_2 + 3H_2 = 2NH_3$$

ammonia

With carbon, hydrocarbons such as benzene and petrol may be formed to a small extent on heating; with sulphur, reaction occurs on heating in presence of a catalyst to form sulphuretted hydrogen, H_2S.

Of the metals, sodium, potassium and calcium all combine directly with dry hydrogen when heated to form the corresponding hydrides,

NaH, KH and CaH_2. These latter compounds react immediately with water to regenerate hydrogen—

$$2NaH + 2H_2O = 2NaOH + 2H_2 \uparrow$$

These hydrides are salt-like in character, e.g. Li^+H^-, due to the formation of an electrovalent linkage. Electrovalency differs from covalency in the manner in which the constituent atoms acquire the "inert-gas" electronic structure. In covalency, the atoms mutually share electrons with each other—

without either atom becoming electrically charged. In electrovalency, electrons are actually transferred from one atom to the other, with the result that the atom which has donated the electron(s) becomes positively charged, whilst the other atom, which has accepted the electron(s), becomes negatively charged. The stability of the molecule as a whole results from the electrostatic attraction between these oppositely charged ions (for a fuller discussion, *see* p. 68). Examples include most salts, such as sodium chloride, NaCl—

Na (atom): electronic structure 2 . 8 . 1. Na^+ (ion): structure 2 . 8.
Cl (atom): electronic structure 2 . 8 . 7. Cl^- (ion): structure 2 . 8 . 8.

The hydrides of the baser metals and metalloids (As, Sb, etc.) are essentially covalent compounds and occur as gases, for example SnH_4, BiH_3 and SbH_3. In general covalent compounds are gaseous or easily volatile (there are exceptions, however) whereas electrovalent or ionic compounds are solid and relatively difficult to volatilize.

Reducing Properties. Hydrogen is a reducing agent by virtue of its affinity for oxygen and for other electronegative elements such as chlorine. Thus—

(i) Hydrogen passed over heated copper oxide forms metallic copper and water

$$CuO + H_2 = Cu + H_2O$$

Many other metallic oxides may be reduced in this way, but *not* those of the reactive metals, K, Na, Ca, Zn and Al.

(ii) When hydrogen is liberated, for example, by the action of an acid on a metal, it probably exists momentarily in the atomic state.

$$Zn + \begin{matrix} Cl^- & H^+ \\ Cl^- & H^+ \end{matrix} \rightarrow (Zn^{++} + 2Cl^-) + 2(H)$$

In this state it is said to be *nascent*, and is a powerful reducing agent. In the normal preparation of the gas, these atoms immediately combine

together to form neutral hydrogen molecules, H_2, but if other compounds capable of reacting with the nascent hydrogen are also present in the solution, such reactions may occur with the highly reactive nascent hydrogen before the latter can combine together to form the much less reactive hydrogen gas. These compounds are then said to be reduced. Examples of the reducing action of nascent hydrogen include the reduction of ferric salts to ferrous salts—

$$FeCl_3 + H = FeCl_2 + HCl$$

of chromic salts to chromous salts, and of potassium chlorate to chloride. These reactions, it should be noted, do not occur at ordinary temperatures when *gaseous* hydrogen is used.

Uses of Hydrogen. Hydrogen is used in many industrial processes, and in recent years its importance has increased due to its use in the hardening of oils. Some of its principle uses are described below.

The Synthesis of Ammonia by the reaction—

$$N_2 + 3H_2 = 2NH_3$$

In the Haber process, the reaction is carried out at 550°C under a pressure of 200 atmospheres in presence of an iron oxide catalyst. The ammonia so produced is used in the manufacture of nitrogenous fertilizers, nitric acid, etc.

The Hydrogenation of Liquid Fats (such as Vegetable and Fish Oils) to Produce Solid Fats. When the oils are heated with hydrogen under pressure in the presence of a nickel catalyst, a chemical reaction occurs in which some of the hydrogen combines directly with the oil molecules. The resulting *hydrogenated oils* have higher melting points than the original oils, and may even be solid substances at ordinary temperatures. Examples include margarine and various proprietary brands of cooking fats.

Synthetic Methyl Alcohol. When a mixture of hydrogen and carbon monoxide is passed over a suitable catalyst at 350–400°C at pressures of 200–600 atmospheres, methyl alcohol is produced—

$$CO + 2H_2 = \underset{\text{methyl alcohol}}{CH_3OH}$$

In the *Fischer-Tropsch synthesis*, the proportion of hydrogen is increased, and the reaction occurs at 180–250°C at atmospheric pressure in the presence of an activated cobalt catalyst. A mixture of aliphatic hydrocarbons ranging from methane to waxes of high molecular weight results. The process was of considerable war-time value to the Germans as a source of lubricants, fatty acids for soap manufacture, detergents and hard waxes.

Hydrogenation of Coal. When coal is heated with hydrogen under the combined action of high pressure, high temperature and the presence of a

catalyst, hydrocarbons related to the petrols are obtained. In the Bergius process, the pressure is of the order of 200–250 atmospheres, the temperature 300–500°C and the catalyst a sulphur resistant material such as molybdenum sulphide. The production of one ton of petrol in this way requires the hydrogenation of about one and a half tons of coal, in addition to that required for hydrogen production, heating, etc.

The Oxy-Hydrogen Blowpipe, which produces temperatures of the order of 2800°C, is used in fusing quartz in the manufacture of fused silica apparatus, and also in working platinum. The flame is produced by supplying hydrogen and oxygen separately to a blow-pipe jet consisting of two concentric tubes, with the oxygen supply inside.

Hydrogen is also used for filling balloons and airships. Its use for this purpose is however limited because of its highly inflammable nature, and in America it is replaced by the heavier but only slightly less buoyant helium gas, which is a natural product.

Atomic Hydrogen

It has been stated that hydrogen gas consists of molecules, each of which contains two hydrogen atoms linked covalently together, and it has also been suggested that the reactivity of hydrogen at temperatures greater than normal is due to the tendency of these molecules to dissociate into very reactive hydrogen atoms—

$$H_2 \rightarrow H + H$$

Langmuir found that if a stream of hydrogen is blown across an electric arc struck between two tungsten electrodes, the very high temperature of the arc causes the hydrogen to dissociate into its atoms, as indicated for example by the very great chemical reactivity and reducing power of the gas as it emerges from the arc. The proportion of hydrogen molecules dissociated increases with increase in temperature, being about 9 per cent at 3000°C and as high as 95 per cent at 5000°C.

When the stream of atomic-hydrogen-rich gas which issues from the arc is allowed to impinge on to a piece of platinum foil, the latter very quickly becomes incandescent. The explanation of this behaviour is simply that the platinum catalyses the recombination of the hydrogen atoms to form hydrogen molecules, and this recombination is accompanied by a considerable evolution of heat energy, as indicated by the equation—

$$H + H = H_2 + 101\,000 \text{ cal.}$$

Intense local heating of the platinum therefore occurs and it becomes incandescent. It has been found possible to use this heating effect to melt some of the most refractory materials, such as tungsten, tantalum and thorium oxide, by allowing the atomic hydrogen to impinge directly

on them as it issues from the arc. The atomic hydrogen blow-pipe, shown in the accompanying diagram works on the same principle, and is used in certain welding operations. It has the additional advantage over other forms of welding torches of providing a reducing atmosphere of hydrogen at the weld, so that very little if any oxidation of the metals being welded can occur.

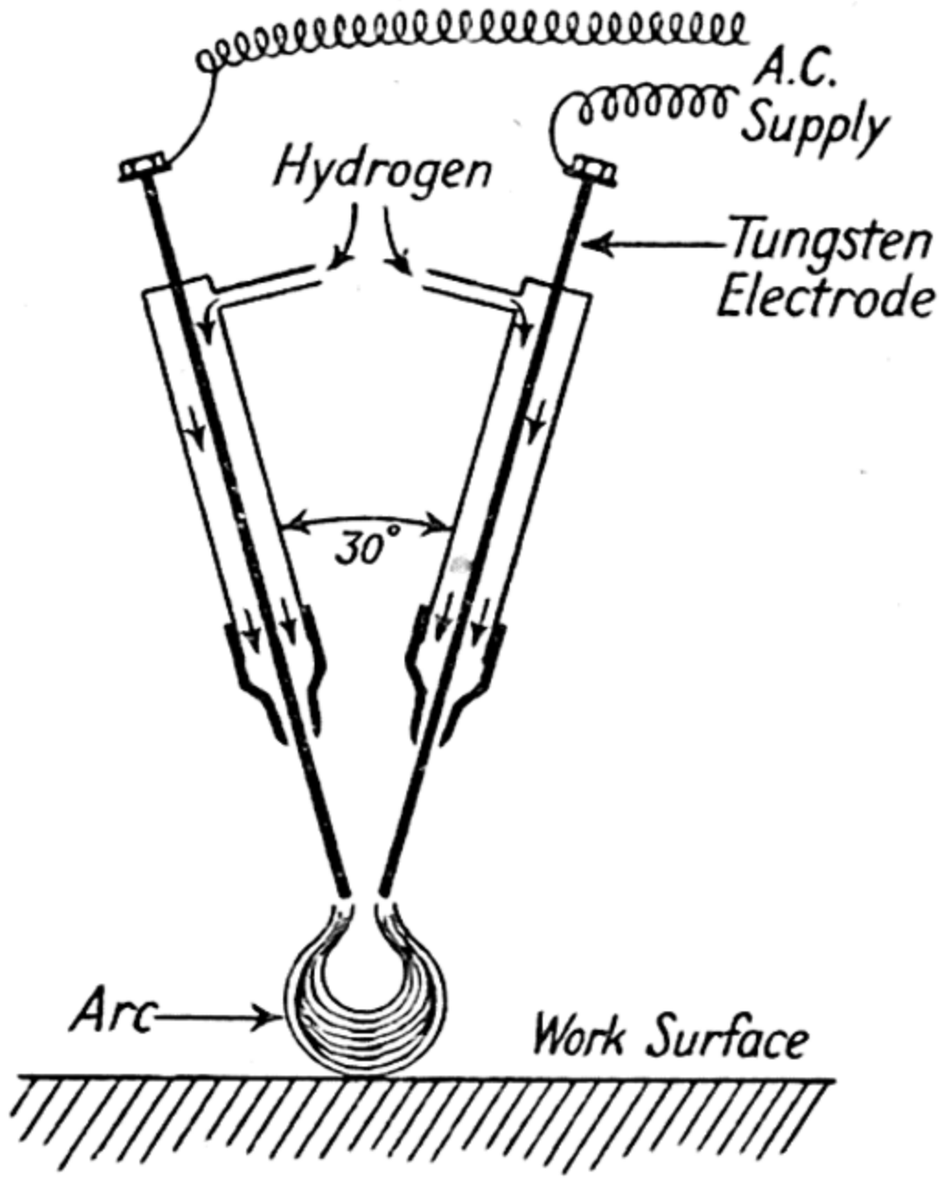
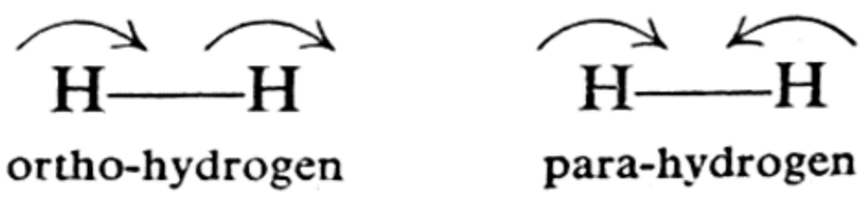


FIG. 135. Atomic Hydrogen Welding

Ortho- and Para-hydrogen

Ordinary hydrogen exists in two forms having slightly different energy contents. Each of these two types of hydrogen molecule is composed of two hydrogen atoms linked together covalently, viz. H:H or H—H. The nucleus of each hydrogen atom, however, is spinning, very much like a top, and the two different forms of molecular hydrogen result from the fact that the hydrogen atoms may unite either with their nuclei spinning in the same direction or in opposite directions. If they are spinning in the same direction, the resulting molecule of hydrogen is anti-symmetrical and is known as *ortho-hydrogen*. If, however, the nuclei are spinning in opposite directions, the resulting molecule is symmetrical and is called *para-hydrogen*. Ortho-hydrogen has slightly more internal energy than para-hydrogen.



Ortho- and para-hydrogen show very little difference in chemical properties. The proportion of each existing together in equilibrium is, however, determined by the temperature. With decrease in temperature, the proportion of para-hydrogen increases, and at absolute zero hydrogen should theoretically exist entirely in the para form.

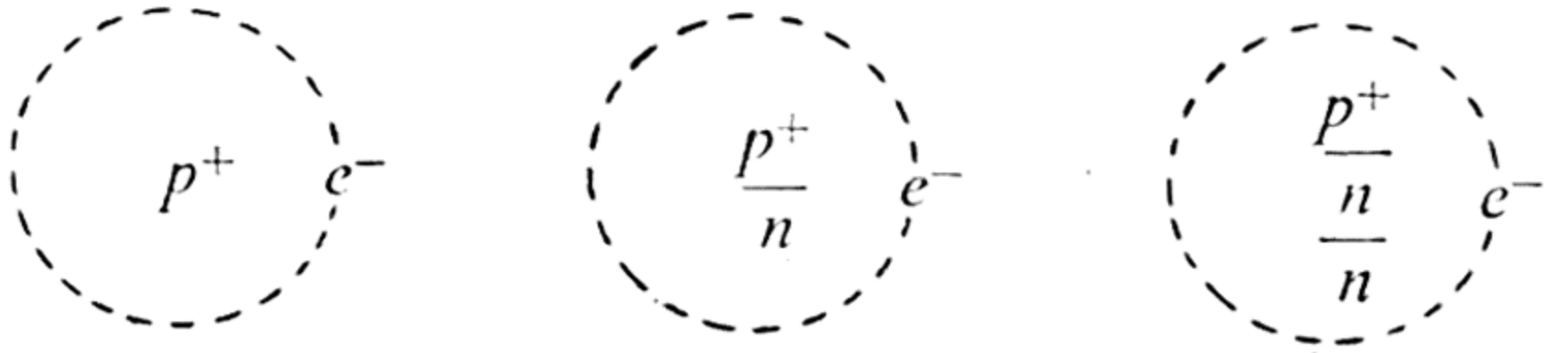
Isotopes of Hydrogen

There are three known isotopes of hydrogen; hydrogen, deuterium and tritium, having atomic weights respectively of one, two and three. The second isotope, deuterium, is present to the extent of about one molecule to 4500 molecules of H_2 in ordinary hydrogen gas, whilst tritium occurs to a very much smaller extent (less than 1 part in 10^7 parts in ordinary hydrogen). Very small quantities of tritium have been detected in the

products of bombarding deuterium (in its compounds, such as deutero-ammonium chloride, ND_4Cl) with a powerful stream of deuterons.

$$^{2}_{1}H + ^{2}_{1}H = ^{3}_{1}H + ^{1}_{1}H$$

The structure of these different isotopes of hydrogen may be represented schematically as follows, in which p^+ denotes a proton with its positive charge, n a neutron with no charge and e^- an electron with its negative charge—



It is seen that deuterium contains one neutron in addition to a positively charged proton in the nucleus, whilst tritium contains two neutrons as well as the proton in the nucleus. The atomic numbers of all three are each one, so that they are correctly regarded as isotopes of hydrogen.

The general rule that the isotopes of an element have almost identically the same properties (for example, chlorine has two isotopes of atomic weights 35 and 37) breaks down with these isotopes of hydrogen because of the relatively much greater change in atomic weight involved. Thus deuterium is twice as heavy as hydrogen, and this relatively large increase in atomic weight modifies the properties of the isotope to an extent which makes it convenient to regard deuterium virtually as a new element.

Heavy water is simply water in which the molecules are composed of D_2O instead of H_2O. Ordinary water contains a small proportion of D_2O molecules, and it is possible by electrolytic methods to isolate this small proportion of heavy water. The electrolytic production, or rather electrolytic isolation, of heavy water from ordinary water is in fact carried out nowadays on a commercial scale. In the following short table are given some comparative figures to show the slight but real difference in properties between ordinary and heavy water—

TABLE 76

Heavy Water Compared with Water

Property	H_2O	D_2O
Boiling point . . .	100·0°C	101·42°C
Freezing point . . .	0·0°C	3·82°C
Specific gravity (20°C) .	0·9982	1·1059
Temperature of max.density	4·0°C	11·6°C

CHAPTER 17

OXYGEN

Occurrence. Oxygen is now known to be the most abundant of all elements, being present in air which is a mixture of oxygen, nitrogen, carbon dioxide and the inert gases, in water in chemical combination with hydrogen, in the silicates in chemical combination with silicon and other elements, and also in the ores of many metals. In the free state, it is one of the more reactive of the gaseous elements, following closely in this respect the very reactive halogens, fluorine and chlorine. In addition, oxygen plays the unique role of being essential to all forms of life, animal, marine and plant. This latter role, however, is more correctly regarded as a special case of the more general phenomenon of combustion, and it is in the attempts to explain this phenomenon that the chemistry of oxygen historically begins.

Historical. The first scientific attempt to explain combustion appears to have been made by two German scientists, Becher (1669) and Stahl (1723), in their celebrated phlogiston theory. Oxygen had not been discovered at that time, and it was supposed that during burning or combustion, something which they called *phlogiston* escaped into the air, leaving a residue or *calx* behind. Thus—

$$\text{Substance} \rightarrow \text{Calx} + \text{Phlogiston}$$

The smaller the calx residue, the greater presumably would be the amount of phlogiston released, and hence substances such as carbon, which left little ash (calx) on burning, were thought to contain a considerable amount of phlogiston. This theory appeared very convincing when applied to such processes as the recovery of metals from their ores (or calces) by heating with carbon, since the latter was very rich in phlogiston.

$$\text{Calx (ore)} + \text{Phlogiston} \rightarrow \text{Metal}$$

Two developments, the first the use of the balance coupled with accurate experimental observation, and the second the discovery of oxygen, contributed to the downfall of the phlogiston theory. The fact, discovered by Lavoisier, that some substances increase rather than decrease in weight when heated in air, for example metallic tin, was not easily explained by the phlogiston theory. It was eventually suggested that phlogiston possessed *levity* or lightness rather than weight, so that its loss would actually be accompanied by an *increase* in weight.

Then came the discovery of oxygen. John Priestley obtained the gas in 1774, although his discovery appears to have been anticipated by a Swedish chemist, Scheele in 1772, who did not, however, publish his results until 1775. Scheele obtained the gas by heating red oxide of mercury, potassium nitrate and various other substances, and called it *vital air* or *fire air*. Priestley isolated the gas by heating mercury oxide (that is, the calx of mercury prepared by gently heating mercury in air) and collected it by the now familiar pneumatic trough technique invented by himself. In this case, the gas was called *dephlogisticated air* and was presumed to result from the removal of phlogiston from the air on heating the calx, thus—

$$\text{Calx} + \text{Air} \rightarrow \text{Metal} + \text{Dephlogisticated air}$$

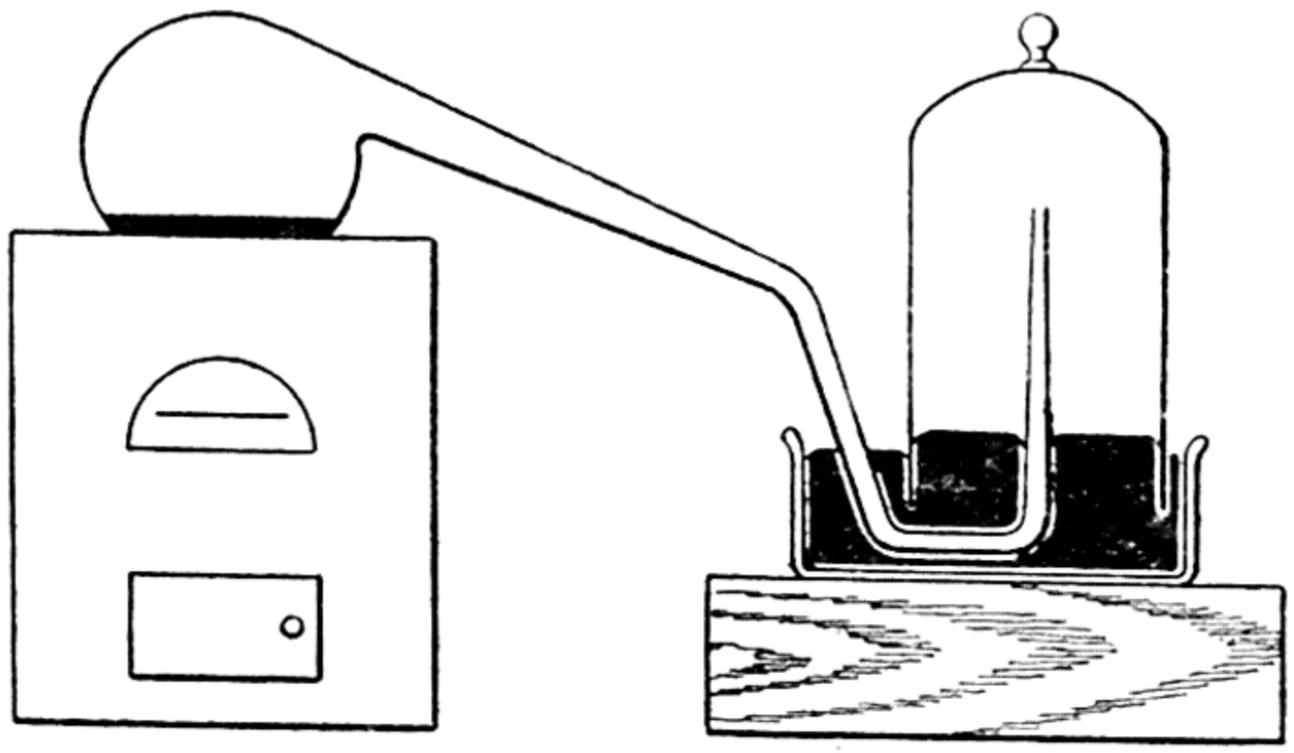


FIG. 136. Lavoisier's Experiment

and since, $$\text{Calx} + \text{Phlogiston} \rightarrow \text{Metal}$$

it follows that

$$\text{Air} - \text{Phlogiston} \rightarrow \text{Dephlogisticated air}$$

This discovery was closely followed by the work of Lavoisier which lead eventually to the rejection of the phlogiston theory as a scientifically acceptable theory of combustion. Having already found that some metals, such as tin, increased in weight when heated in air, he proceeded as a result of a visit by Priestley to carry out the following experiment.

A weighed amount of mercury was heated (over a charcoal fire) in a retort connected to a bell-jar of air confined over mercury as shown in the diagram. After keeping the mercury near the boiling point for some twelve days, he found that no further decrease occurred in the volume of the air in the bell-jar. The change in this volume was recorded and the retort broken open. The red calx of mercury was then carefully collected and placed in a very small tube connected to a similar bell-jar, now filled with mercury, as in the first part of the experiment. On heating the calx to a much higher temperature than before, a gas was collected which was

found to have the same properties as Priestley's dephlogisticated air and in addition to be equal in volume to the decrease recorded in the first part of the experiment. Lavoisier thus showed that a gas could be removed from air by combining with mercury (which accordingly increased in weight) and that this gas could be regenerated by later reheating the calx. Lavoisier named the gas *oxygen* and called the calx, mercury *oxide*. The reactions involved were—

Mercury + Oxygen → Mercury oxide (first experiment)

Mercury oxide → Mercury + Oxygen (second experiment)

and not, as the phlogistonists supposed—

Mercury → Oxide (calx) + Phlogiston

Calx + Air → Metal + Dephlogisticated air

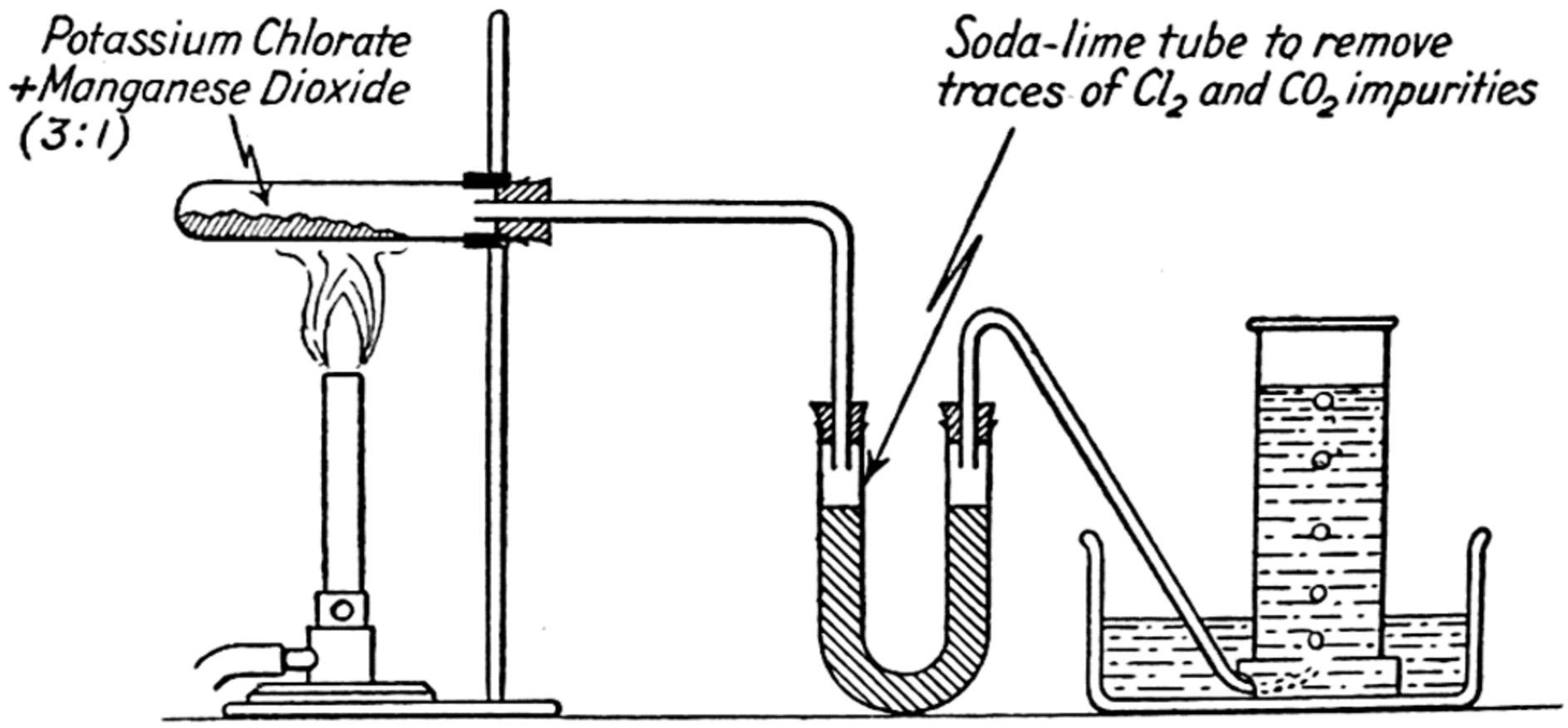


FIG. 137. Preparation and Collection of Oxygen

Laboratory Methods of Preparation. Many methods are available for obtaining oxygen from compounds containing it; five of these methods are described below.

Action of Heat on Potassium Chlorate. The usual laboratory method is to heat a mixture of potassium chlorate and manganese dioxide, preferably in a hard glass tube, and collect the gas in the usual way over water as shown in the accompanying diagram. It is of practical importance to note that the use of manganese dioxide containing carbonaceous impurities often leads to serious explosions (due to the explosive nature of potassium chlorate-carbon mixtures). The dioxide should accordingly be tested by heating a small portion with potassium chlorate and, if unsatisfactory, the remaining manganese dioxide should be heated alone in air for some time before attempting the preparation.

The manganese dioxide functions in this reaction as a *catalyst*; it speeds up the rate at which the potassium chlorate decomposes and so permits

the reaction to be carried out at a much lower temperature than would be the case if it were absent; it is chemically unchanged at the end of the reaction, and may in fact be recovered by dissolving up the potassium chloride, KCl, and any undecomposed potassium chlorate which may remain. The precise mode of action of the manganese dioxide is uncertain; it is possible that it first reacts with the potassium chlorate to form a higher manganese oxide, such as Mn_2O_7, which is unstable at the temperature of the preparation and so decomposes to reform manganese dioxide and liberate oxygen. Such a cycle of reactions could occur until all the potassium chlorate had been decomposed, and this explanation appears to be supported by the decreased particle size of the manganese dioxide recovered at the end of the experiment. The cycle of reactions would be—

$$KClO_3 + 2MnO_2 = (Mn_2O_7) + KCl$$
$$(2Mn_2O_7) = 4MnO_2 + 3O_2 \uparrow$$

Since, however, the manganese dioxide remains chemically unchanged at the end of the reaction, it is sufficient to express the net reaction by the simple equation—

$$2KClO_3 = 2KCl + 3O_2$$

Other substances which might be used as catalysts include the oxides of cobalt, nickel and iron.

In the absence of manganese dioxide, the potassium chlorate first melts to a clear liquid at about 340°C. Approximately 10°C higher, this liquid appears to boil due to liberation of oxygen by the reaction

$$2KClO_3 = 2KCl + 3O_2$$

At the same time, potassium perchlorate is also formed—

$$4KClO_3 = 3KClO_4 + KCl$$

and this requires a still higher temperature before it too decomposes to liberate oxygen—

$$KClO_4 = KCl + 2O_2$$

Action of Heat on Oxides. Certain oxides, that is, compounds of elements with oxygen, may decompose on heating to liberate oxygen. Such oxides include those of the less reactive metals, silver, mercury, and also most peroxides or superoxides, (Pb_3O_4, MnO_2, BaO_2, etc.)—

$$2Ag_2O = 4Ag + O_2$$
$$2PbO_2 = 2PbO + O_2$$
$$2HgO = 2Hg + O_2$$
$$2BaO_2 = 2BaO + O_2$$

Note, also, Lavoisier's method of using mercury to obtain oxygen from

the air. The barium peroxide reaction is the basis of the now obsolete Brin process for obtaining oxygen commercially from the air. (*See* below.)

Action of Heat on Other Oxy-salts. Certain oxy-salts also liberate oxygen when heated; for example permanganates, nitrates, chlorates, etc.

$$2KNO_3 = 2KNO_2 + O_2$$
$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$
$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

Action of Water on Solid Sodium Peroxide, Na_2O_2. This reaction may be carried out by dropping water from a tap-funnel on to solid sodium peroxide in a dry flask and collecting the liberated oxygen over water in the usual way.

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2$$

The reaction depends upon the intermediate formation of hydrogen peroxide, H_2O_2, which is decomposed by the heat of the reaction and by the alkalis present.

$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2$$
$$2H_2O_2 = 2H_2O + O_2$$

Electrolysis of Barium Hydroxide, $Ba(OH)_2$, using nickel electrodes liberates pure oxygen at the anode and hydrogen at the cathode (*see* p. 240).

Manufacture of Oxygen. Commercially oxygen is nowadays obtained from air by the fractional distillation of liquid air. Formerly, it was obtained on a large scale by the now obsolete Brin's process.

Brin's Process. If barium oxide is heated in air at about 500°C, it is oxidized to barium peroxide. At 800°C however the BaO_2 decomposes to reform BaO and liberates oxygen, thus—

$$2\ BaO + O_2\ (air) = 2\ BaO_2\ (at\ 500°C)$$
$$2\ BaO_2 = 2\ BaO + O_2\qquad (at\ 800°C)$$

By using air purified from suspended matter, carbon dioxide and other substances which might react permanently with the barium oxide under these conditions, the cycle of operations might theoretically be repeated indefinitely to produce oxygen in quantities limited only by the capacity of the manufacturing plant. It was later found that the same result could be obtained by keeping the temperature constant and instead varying the pressure, a fact which was put to practical use in the Brin process. The temperature was maintained constant in the region of 700°C, and purified air pumped in under a pressure of about 10 lb/in.^{2}; the BaO changed to BaO_2. The pumps were then reversed to form a partial vacuum, when the BaO_2 decomposed by the reverse reaction. The gas so produced was pumped off and collected; it contained about 90 to 96 per cent of oxygen and from 4 to 10 per cent of nitrogen. Barium peroxide is however still prepared by the first stage of this process, and is important as a source of hydrogen peroxide (q.v.).

Modern Process. The present-day process for obtaining oxygen from the air falls into two stages—

(*a*) The production of liquid air, and
(*b*) the fractional distillation of this liquid air.

Production of Liquid Air

In 1823 Michael Faraday reviewed the state of knowledge concerning the liquefaction of gases and described his own successful attempts to liquefy chlorine, hydrochloric acid, sulphur dioxide, sulphuretted hydrogen, carbon dioxide, nitrous oxide and cyanogen by cooling the gases under pressure. Gases such as hydrogen, oxygen, nitrogen, nitric oxide and carbon monoxide, could not be liquefied by this method and came to be referred to as *permanent* gases.

The discovery of the Joule-Thomson effect, i.e. that gases suffered a cooling effect when allowed to expand through an orifice from a high pressure to a low pressure (with hydrogen the reverse effect occurs unless the hydrogen be first cooled below its inversion temperature), led in 1895 to W. Hampson in England and to C. Linde in Germany devising methods for the liquefaction of air. Air at about 150 atmospheres pressure was passed through a coil of closely wound small-bore copper pipe, and allowed to expand freely through a valve placed at the end. The slightly cooled air so produced (Joule-Thomson effect) was then returned through an outer tube concentric with the former delivery tube, thereby cooling the incoming compressed air. This latter in expanding at the jet suffered a further cooling effect and then as before cooled the incoming compressed air. The returning air was then passed to the pumps where it was again compressed and returned with more air to the inner tube from which it eventually again expanded at the jet. The process thus depended upon a gradual lowering of the temperature by counter-current cooling of the incoming gas by outgoing gas to the air liquefaction temperature, when drops of liquid air formed from the jet.

In the later Claude modification of the process, the adiabatic cooling effect as above is considerably increased by making the expanding gas perform work in a form of expansion engine. In the performance of this work, the air loses an equivalent amount of heat energy and becomes cooler. In modern plant which employ this system, the Joule-Thomson effect is responsible for about 30 per cent of the cooling, the other 70 per cent resulting from the performance of external work. The energy recovered in this way is used to generate electrical power to supplement that used in the earlier compression of the air.

Fractional Evaporation or Distillation of Liquid Air

The next stage in the process is to recover oxygen from the liquid air. When liquid air is allowed to evaporate, it might be expected that nitrogen

which has its boiling point some 12·8°C lower than that of oxygen (— 195·8°C as compared with — 183°C for oxygen) would evaporate first leaving liquid oxygen behind. This expectation however is not so simply realized in practice. It is a fundamental fact that when a mixture of two liquids is distilled the vapour formed always contains a higher percentage of the more volatile constituent (in this case, nitrogen), and the remaining liquid a correspondingly higher proportion of the less volatile constituent (oxygen). If this vapour is condensed and then redistilled, the new vapour will in the same way contain an increased proportion of the more volatile constituent. The number of times this condensation-evaporation process has to be carried out before complete separation is effected is largely determined by the difference in boiling points of the two liquids. The smaller this difference, the greater the number of stages. The student will thus appreciate that in the case of the separation of nitrogen from oxygen in liquid air, a large number of such separate distillations is necessary. The process whereby a large number of separate evaporation-condensation reactions may be carried out in one operation is known as *fractional distillation*. This process, the basis of the separation of oxygen from liquid air, is most easily described with reference to a simple fractionating column of the type used in ordinary laboratory practice.

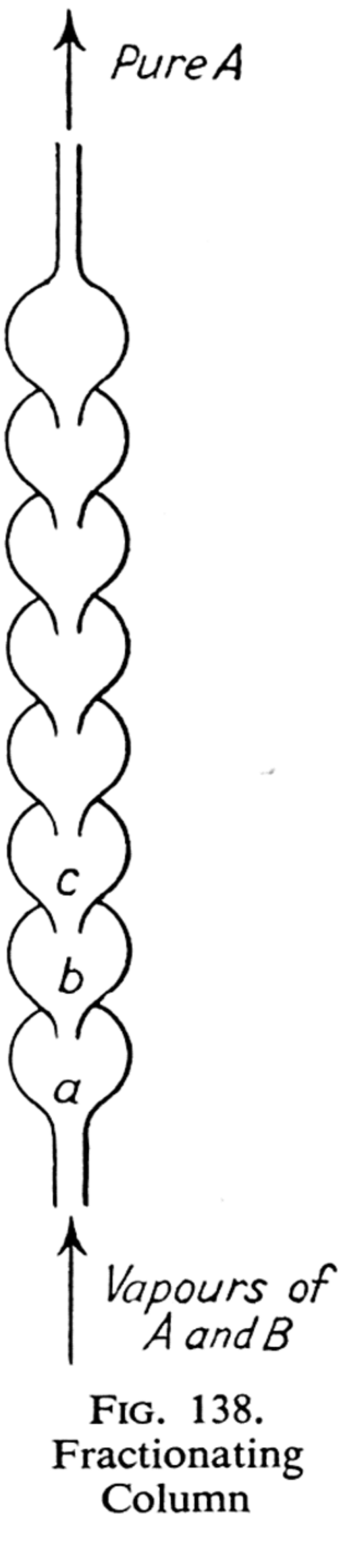


FIG. 138. Fractionating Column

The diagram shows the separation of two liquids *A* and *B* by fractional distillation, in which liquid *A* has a lower boiling point and is therefore more volatile than liquid *B*. The vapour leaving the flask is richer in *A*, and condenses at *a*. This *A*-enriched liquid eventually redistils, and condenses at *b* with an increased proportion of *A*, and at the same time a liquid poorer in *A* returns to the flask. This process of distillation and condensation continues throughout the fractionating column, and results in a progressively increasing proportion of liquid *A* in the vapour with ascent of the column, and a corresponding increase in the proportion of liquid *B* in the residual liquid in the flask. With an efficient fractionating column of this type a practically complete separation of the two liquids may be obtained.

The principle of fractional distillation is applied in all the commercial processes for obtaining oxygen from liquid air, whether based on the Linde-Hampson or modified Claude processes. In the modern plant the two stages of liquefying air and fractional distillation of the liquid air

are combined in one plant. The diagram below shows in Fig. 139 a flow sheet for the whole process, and in Fig. 140 the Linde liquefier and double column rectifier. This double column rectifier or fractionating column is so arranged that the reflux condenser of one tower serves as the reboiler of the other, and embodies as an essential feature a difference in pressure between the upper and lower column, as a result of which pure oxygen evaporating on one side of the column can bring about liquefaction of pure nitrogen on the other. Since the normal boiling point of nitrogen is lower than that of oxygen, the pressure in the lower column must be higher than that in the upper column. If the upper column works at one atmosphere pressure, the minimum pressure for the lower column is 3·6

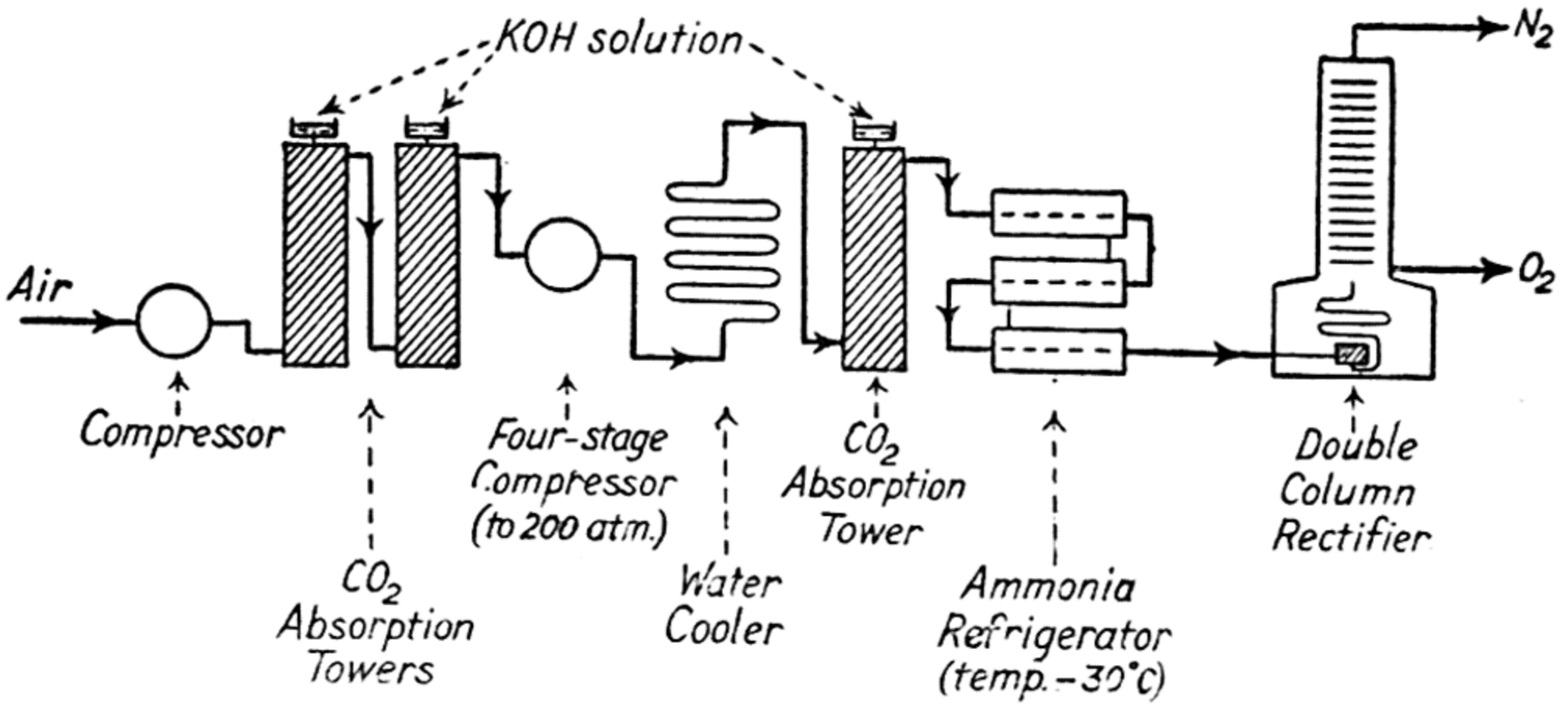


FIG. 139. Flow Sheet for the Production of Oxygen from Air by Liquefaction-Distillation Process

atmospheres, since at this point the boiling point of oxygen coincides with that of nitrogen.

Referring to Fig. 140, the cooled and compressed air enters counter-current to the outgoing nitrogen through a heat interchanger (*a*). The cold compressed air, which is still warmer than the liquid in the column, passes through the coil in the bottom of the column (*b*) and thus supplies the heat necessary for the vaporization in this section. The colder compressed air, so produced, then expands at the valve (*c*) from 200 atmospheres to 4–6 atmospheres pressure, being sufficiently cooled here to liquefy by the Joule-Thomson effect. The liquid air then flows downwards through the lower column against the rising vapours of its own most volatile constituent, nitrogen. The less volatile constituent, oxygen, thus collects at the bottom of the column, at (*d*). Part is vaporized to carry on the fractional distillation, but any accumulation of this liquid is forced, by the pressure drop between (*b*) at 4–6 atmospheres and (*e*) at 1–1·3 atmospheres, to pass through the valve (*f*) to the upper rectifying column, entering at (*g*). This 40 per cent liquid oxygen passes down the upper

column losing its more volatile nitrogen until it accumulates at (*h*) whence it is drawn off as liquid oxygen of 99 and more per cent purity.

The nitrogen in the liquid air entering at *c* as the more volatile constituent gradually volatilizes, passes upwards and is cooled and condensed by the tubes and dome of (*j*). The nitrogen-rich liquid which collects here is moved to the top of the upper column, the liquefaction resulting from the increased pressure obtaining in the lower system. As this liquid passes down the

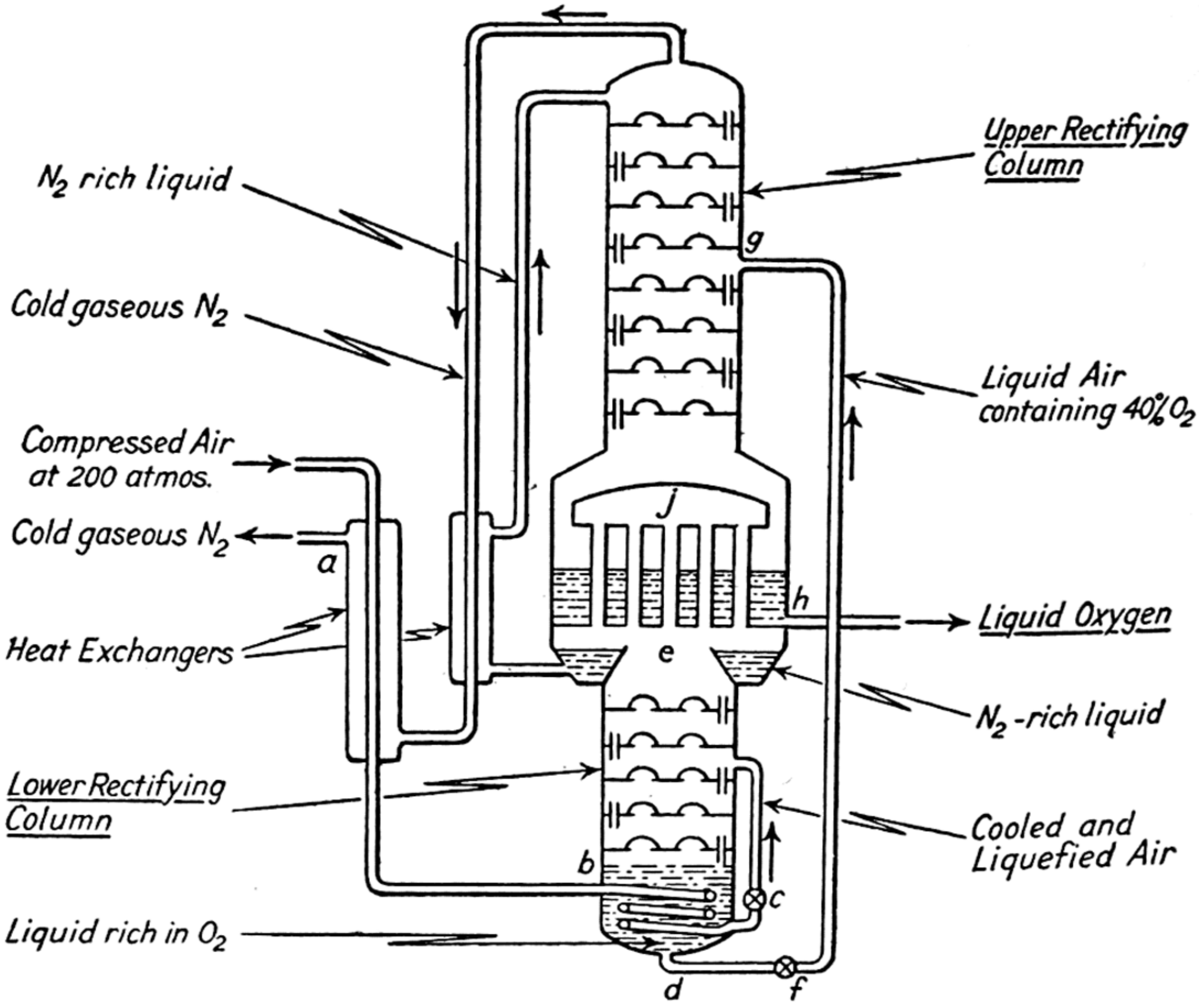


FIG. 140. Linde Liquefier and Double Column Rectifier

upper column, the more volatile nitrogen passes off through the heat interchanger (*a*).

Action of Sodium Manganate on Air. A recent chemical process has been patented in America for obtaining oxygen of high purity from air. Air and steam are passed alternately over a contact mass consisting of sodium manganate (Na_2MnO_4) which collects oxygen from the air and subsequently releases it to the steam.

Physical Properties. Oxygen is a colourless, odourless gas, which is difficult to liquefy and solidify. It may be liquefied at $-183°C$ to a pale blue mobile liquid which is strongly attracted by a magnet, and may also

be solidified, for example, by cooling the liquid in a jet of liquid hydrogen, when it forms a snow-like pale-blue solid. At 0°C and 760 mm pressure, the density of the gas is 1·429 g/litre, that is, approximately sixteen times as heavy as hydrogen. It is sparingly soluble in water; at 0°C 100 volumes of water dissolve 4·9 volumes of oxygen. This solubility, although small, is however extremely important, since fish depend upon dissolved oxygen for respiration, polluted water supplies may through the action of dissolved oxygen again be made potable, and other waste products of animal, marine or vegetable origin present in water may be converted by bacterial oxidation into harmless products or foodstuffs for marine life. Oxygen is slightly more soluble in water than is nitrogen (0·049, cf. 0·024 c.c./c.c. of water at 0°C and 760 mm pressure), so that although air contains approximately 21 per cent of oxygen by volume, the gas recovered by boiling water contains the increased proportion of about 34 per cent of oxygen by volume.

Chemical Properties. The oxygen gas molecule is composed of two atoms of oxygen, and is accordingly represented in chemical equations by the formula O_2. Other gaseous elements, such as nitrogen, hydrogen, fluorine and chlorine, but not the inert gases (helium, neon, argon, etc.) also exist in the diatomic molecular state, having the formulae N_2, H_2, F_2 and Cl_2 respectively. The gases do not therefore consist of the element in the very reactive atomic state, and this fact accounts in general for the stable existence of these gases at ordinary temperatures. Chemical reaction with other elements or compounds usually requires some change in the conditions (for example by raising the temperature) before the reactions can take place, Reactivity is greatest with fluorine, less with chlorine, oxygen, hydrogen and nitrogen in this order, and nil with the inert gases.

In the preceding paragraph two statements have been made which require some explanation before proceeding to discuss the chemical properties of oxygen in detail. These statements were—

(i) that the gases, oxygen, hydrogen, etc., exist as diatomic molecules, whereas the inert gases occur in the atomic state, that is, as monatomic molecules, and

(ii) that some change in the conditions are in general necessary before oxygen, hydrogen, etc., react chemically with other elements or compounds.

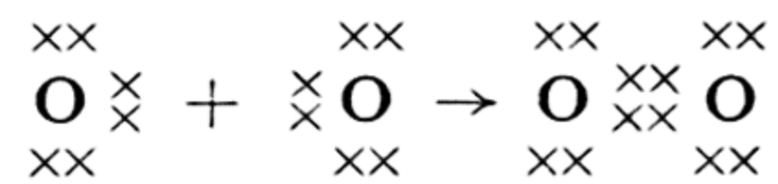
Considering first the statement regarding the molecular state of the gaseous elements, the important point to note is that the inert gases exist simply as free atoms. The modern theory of chemical reactivity is based on this fundamental fact. It is argued that since these elements exist in the atomic state and are devoid of chemical reactivity, they must possess a particularly stable electronic structure. The work of Rutherford

has shown that the atom of each element is composed of two parts; the central nucleus or core composed of protons and neutrons, and the external, or extranuclear, orbital electrons. The mass of the atom is determined almost entirely by the nucleus, but the chemical reactivity of the element is determined by the number and in particular by the arrangement of these extranuclear electrons. In the case of the inert gases, these electrons have a particularly stable electronic structure, viz.—

Inert Gas	*Electronic structure*					
Helium	2					
Neon	2	8				
Argon	2	8	8			
Krypton	2	8	18	8		
Xenon	2	8	18	18	8	
Radon	2	8	18	32	18	8

The electronic structure of the inert gases is discussed in more detail on pp. 351 to 353, to which reference might well be made by the student at this stage. For the purpose of the present discussion it is sufficient to add that the non-inert elements, nearly ninety in all, are chemically reactive because they possess more (or less) electrons than the nearest inert gas. By reaction with themselves, or with other elements, they lose (or gain) the necessary electrons and so acquire the "inert-gas" electronic structure. Chemical activity thus results from the tendency of an atom to acquire the "inert gas" electronic structure.

The oxygen atom with the electronic structure "2·6" requires two additional electrons if it is to acquire the neon structure. In the case of the oxygen molecule, O_2, each atom shares two electrons with the other, whereby each acquires the helium structure. Considering only the outermost incomplete electronic orbit, this sharing may be depicted—



that is O=O or O_2 (but *see* p. 72).

As long as this molecule is not disrupted in any way, as discussed below, it will be perfectly stable. Indeed, at ordinary temperatures, oxygen gas is quite stable; it occurs in the atmosphere, and is stored for commercial use under very high pressures in steel cylinders.

Considering next the second statement, it will be apparent that the gas oxygen will not react chemically with other elements unless it suffers some dissociation into free atoms. It will be seen below that oxygen reacts readily with most of the elements if these are heated sufficiently. The primary reason for this fact is that the higher the temperature, the

more easily will the oxygen molecule dissociate. The molecule of oxygen possesses energy of translation (i.e. of motion), of rotation, and also of vibration. Increasing the temperature increases all three of these, so that the vibrational movement of the oxygen may become so violent that the molecule dissociates. In Fig, 141 the maximum and minimum vibrational distances apart of the oxygen atoms are depicted as a function of increasing energy content. When the molecule acquires the energy *D* it will dissociate into free atoms. Not all the molecules, however, possess the same energy content. Some will possess very much more, and others very much less than the average energy, and Fig. 142 shows the Maxwellian distribution of energy amongst the molecules at a particular temperature. Clearly,

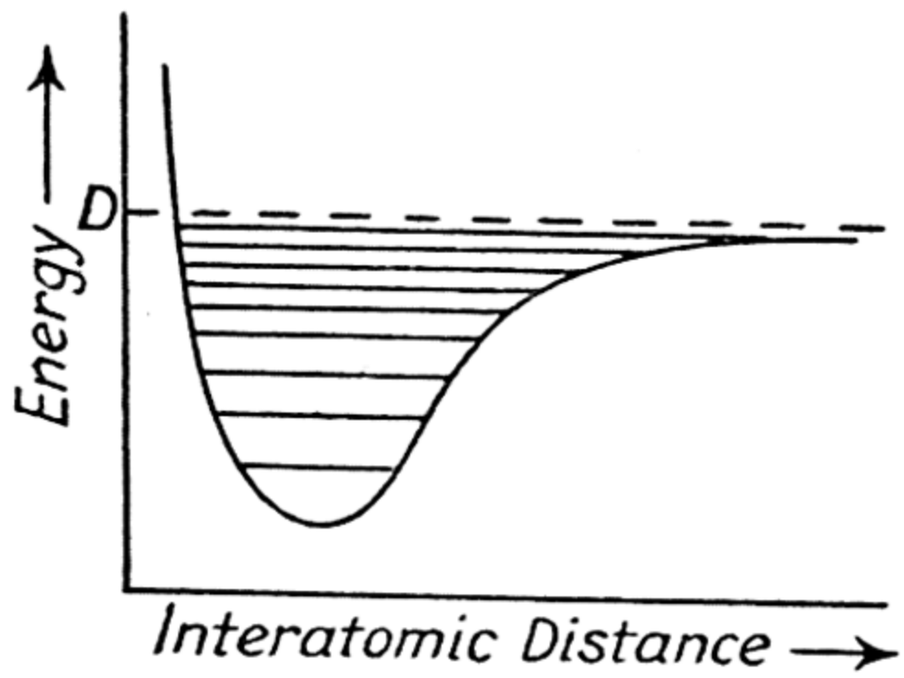


FIG. 141. Potential Energy as a Function of Interatomic Distance for a Diatomic Molecule

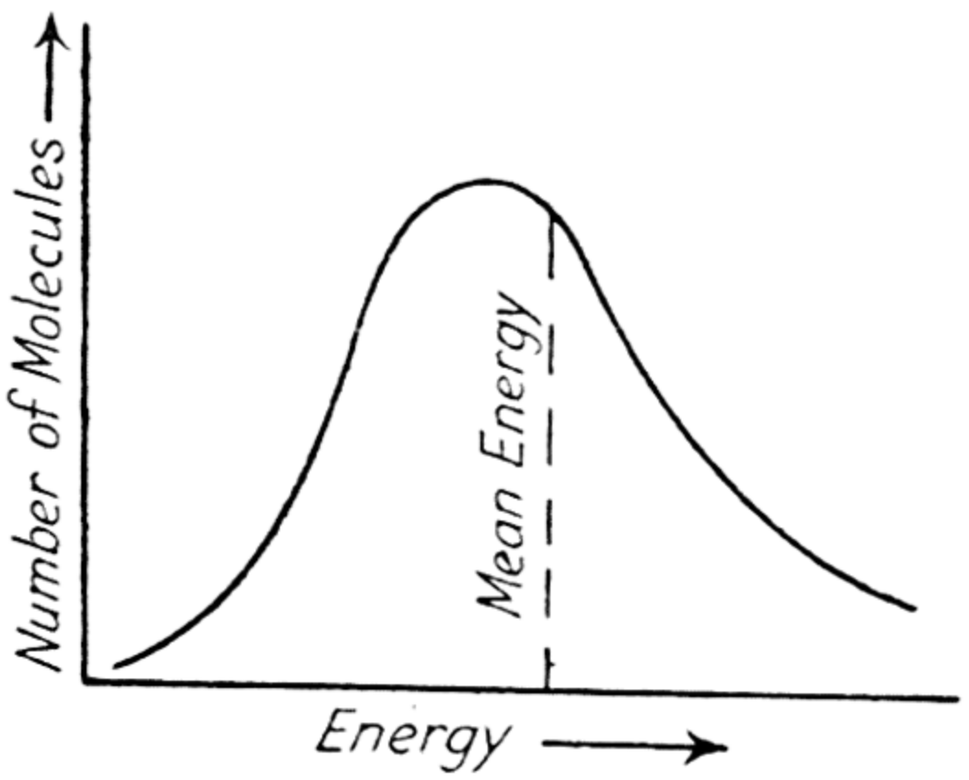


FIG. 142. Distribution of Energy amongst the Molecules of a Gas

a very small number of molecules (those having the highest energy content) will begin to dissociate at temperatures appreciably less than that necessary for the dissociation of the bulk of the molecules. It is to this small dissociation at moderate temperatures that the reactivity of oxygen is to be attributed. The heat liberated as a result of the reaction of these atoms with other elements present, leads to further dissociation of other oxygen molecules, and to increasing reactivity. Fluorine and chlorine are more reactive than oxygen because they require less energy before they dissociate; their dissociation energies are smaller. Nitrogen requires much more, and so is often referred to as *inert*, although the student will now appreciate that under favourable conditions nitrogen may also and does react quite vigorously. No dissociation into electron-deficient atoms can possibly occur with the monatomic inert gases, and these are accordingly inert at all temperatures.

Other factors which may affect the reactivity, in addition to that of temperature, may now briefly be mentioned. These include—

(i) The presence of a catalyst, which speeds up the rate of a reaction.

For example, platinum which promotes combination between hydrogen and oxygen at ordinary temperatures.

(ii) The reactivity occasioned by one of the reacting molecules not possessing a full complement of electrons. Nitric oxide is an example of such a compound; it reacts with oxygen immediately at ordinary temperatures.

These and other methods of promoting reactivity will be discussed in some detail as examples occur in the text.

Returning to the chemical properties of oxygen, it may be said that oxygen is a very reactive element. Under the right conditions, it will combine directly with practically all of the elements, with the exception of the inert gases and fluorine, although various fluorides of oxygen may be prepared indirectly. The more reactive metals, from potassium to tin in the electrochemical series (*see* p. 272), all burn strongly when heated in oxygen to form the corresponding oxides; the less reactive metals, copper, mercury, etc., also combine but without burning when gently heated in the gas. The non-metallic elements, sulphur and phosphorus, if ignited and plunged into a gas jar of oxygen burn brilliantly to form sulphur dioxide and phosphoric oxide respectively, the flame in the case of the sulphur being of a rich blue colour. Glowing charcoal (carbon) similarly glows quite strongly when plunged into oxygen, the product of this reaction being carbon dioxide. In all these reactions some form of heat energy has to be supplied to initiate the reaction, but once started the exothermic nature (that is, heat is generated) of the reaction ensures an increasing temperature and ease of reaction.

Certain compounds however react with oxygen at ordinary temperatures, and the reason for this reactivity must be sought in the electronic structure of the compound. Thus nitric oxide reacts immediately with oxygen at ordinary temperature to form the brown gas, nitrogen peroxide—

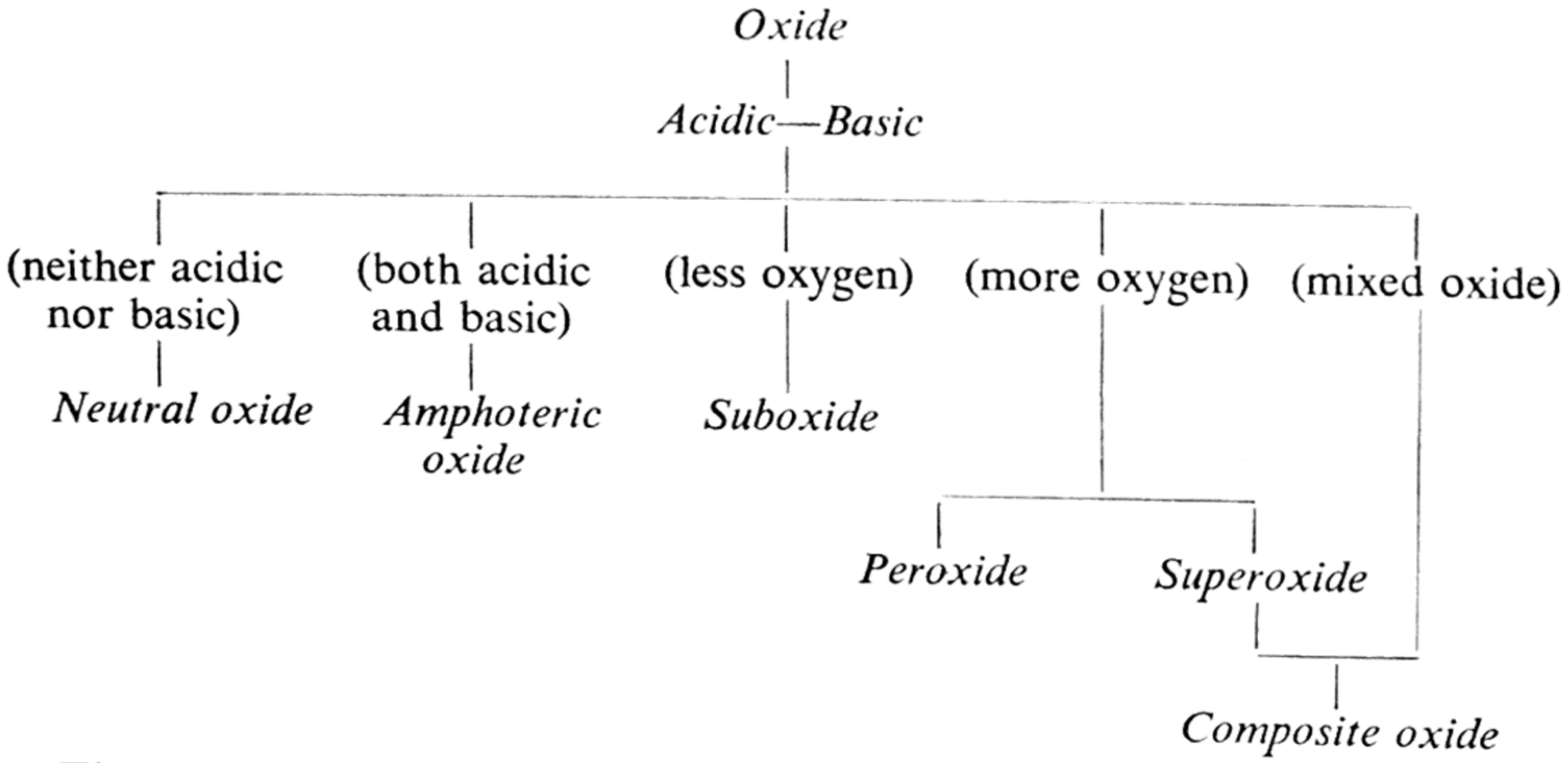
$$2NO + O_2 = \underset{\text{peroxide}}{\underset{\text{nitrogen}}{2NO_2}}$$

Various suboxides, such as lead suboxide, similarly combine readily with oxygen at ordinary temperatures. In all these cases, the reacting compound is now known to have an incomplete electronic structure, and in combining with oxygen it acquires its full complement of electrons at the expense of the oxygen-oxygen linkage.

CLASSIFICATION OF OXIDES

The name *oxide* is given to those compounds which contain only oxygen and one other element. Thus magnesium oxide MgO is an oxide, but magnesium sulphate $MgSO_4$ is not. The following table sets out the possible

types of oxides so as to show their relation to each other, the correct name of the oxide being given in each case in italics.



The term *normal oxide* is sometimes used in a general sense to describe those oxides in which the element is showing its normal valency.

Acidic Oxides. Oxides which react with bases or alkalis to form salts are called acidic oxides. They include the normal oxides of the non-metals, for example CO_2, SO_2, B_2O_3, SiO_2, all of which may dissolve in water to form acids, e.g.—

$$SO_2 + H_2O = \underset{\text{sulphurous acid}}{H_2SO_3}$$

Sometimes the acid is however ill-defined or unknown (e.g. carbonic acid, silicic acid, etc.).

Other higher oxides of the non-metals are however also acidic, for example, nitrogen peroxide, sulphur trioxide and phosphoric oxide.

Basic Oxides. Basic oxides, and bases and alkalis, are characterized by their negative property of destroying or reversing the effects caused by acids. A basic oxide is therefore an oxide which will react with an acid to form a salt and water. The normal oxides of metals, for example, magnesium oxide, are predominantly basic.

$$MgO + H_2SO_4 = \underset{\text{magnesium sulphate}}{MgSO_4} + H_2O$$

Neutral Oxides. Oxides which are neither acidic nor basic are termed neutral oxides. Examples include, nitrous oxide, N_2O, carbon monoxide, CO, but not water which according to the modern theory of acids and bases is more strictly amphoteric.

Amphoteric Oxides. Oxides which may under the appropriate conditions of reaction, behave either as an acidic oxide or as a basic oxide are termed

amphoteric. The usual examples quoted are zinc oxide and aluminium oxide, but most of the metals which occur in two or more valency states show increasing amphoteric behaviour the higher the oxide, the acidic properties becoming predominant in the highest oxides.

Base	+ Acid	= Salt	+ Water	
ZnO	+ H_2SO_4	= $ZnSO_4$	+ H_2O	(basic action)
2NaOH + ZnO		= Na_2ZnO_2	+ H_2O	(acidic action)
Al_2O_3	+ 6HCl	= $2AlCl_3$	+ $3H_2O$	(basic action)
2NaOH + Al_2O_3		= $2NaAlO_2$	+ H_2O	(acidic action)

Modern opinion inclines to the view that the solution of aluminium oxide (or hydroxide) in an alkali results from the peptizing action of the alkali to form a colloidal solution of aluminium hydroxide, a view which explains the current industrial practice of purifying aluminium hydroxide by stirring a little freshly precipitated aluminium hydroxide into the sodium hydroxide solution, whereby the whole of the aluminium hydroxide is precipitated. The formula of sodium aluminate, however, if the older views are accepted, is most easily obtained by the student, if he rewrites the Al_2O_3 as $Al(OH)_3$, and then rearranges this so that it *looks like an acid*—

$$Al(OH)_3 \rightarrow H_3AlO_3 \text{ or } \rightarrow HAlO_2 + H_2O$$

whence

Base	+ Acid	= Salt	+ Water
NaOH + $HAlO_2$		= $NaAlO_2$	+ H_2O
		sodium aluminate	

Suboxides. Certain oxides contain less oxygen than the normal oxides. They are usually unstable and are known as suboxides. Examples include carbon suboxide, C_3O_2, lead suboxide, Pb_2O, and sodium suboxide, Na_4O. Since, however, carbon suboxide is obtained by dehydrating malonic acid, it may also be regarded as an acidic oxide—

$$CH_2(COOH)_2 - 2H_2O = C_3O_2$$

Higher Oxides. Those oxides which possess more oxygen than the normal oxides are known as higher oxides, and may be divided into two classes based on their slightly different properties. The true *peroxide*, for example sodium peroxide and barium peroxide, liberate hydrogen peroxide when treated with a dilute acid—

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

The oxides, such as manganese dioxide, lead dioxide, etc, which do not liberate hydrogen peroxide in this way are termed *superoxides*. Both

classes evolve oxygen on heating alone and also with concentrated sulphuric acid, and liberate chlorine on heating with concentrated hydrochloric acid. The peroxides are now known to be electrovalent in character, whereas the superoxides are essentially covalent—

Peroxide: $Na^+ \overline{O} - \overline{O} Na^+$ Superoxide: $O=Mn=O$

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

Composite Oxides. Those oxides which behave in reactions as if they were mixtures or compounds of two oxides of the same metal are termed composite oxides. It must be emphasized, however, that the composite oxide is not a mere mechanical mixture of two oxides. Examples include—

Red lead, Pb_3O_4 $(2PbO + PbO_2)$
Ferroso-ferric oxide, Fe_3O_4 $(FeO + Fe_2O_3)$
Trimanganese tetroxide, Mn_3O_4 $(2MnO + MnO_2)$

Thus red lead with dilute nitric acid forms a solution of lead nitrate from the PbO portion of the oxide, and leaves the PbO_2 as a brown residue—

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + 2H_2O + PbO_2$$

OXIDATION AND REDUCTION

In its simplest form, the term *oxidation* implies the addition of oxygen. Thus, when sulphur is burnt in air or in oxygen, it is *oxidized* to sulphur dioxide—

$$S + O_2 = \underset{\text{sulphur dioxide}}{SO_2}$$

All the reactions of oxygen enumerated above are consequently oxidation reactions. The hardening of paints containing linseed oil, the burning of fuels such as coal, coke, etc., the explosion of petrol vapour-air mixtures in the internal combustion engine, and the part played by oxygen in animal respiration, are all examples of oxidation reactions in everyday life.

Sometimes the oxidation of an element or compound involves the removal of oxygen from some other compound. Thus when burning magnesium continues to burn in carbon dioxide gas, or in nitrous oxide gas, the carbon dioxide (and nitrous oxide also) loses oxygen.

$$2Mg + CO_2 = 2MgO + C$$
$$Mg + N_2O = MgO + N_2$$

This removal of oxygen is termed *reduction*, and we say that the carbon dioxide has been *reduced* to carbon. At the same time, of course, the

magnesium has been oxidized to magnesium oxide. Thus oxidation and reduction are complementary. Other examples include—

$$CuO + H_2 = Cu + H_2O$$

(hydrogen gas passed over heated copper oxide)

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

(a reaction which occurs in the blast furnace)

In the first example, the oxidation of hydrogen is accompanied by the reduction of the copper oxide; in the second, the oxidation of the carbon monoxide reduces the ferric oxide to metallic iron.

Those substances which produce oxidation are referred to as oxidizing agents, and conversely reducing agents are those substances which promote reduction. Thus in the preceding examples, hydrogen and carbon monoxide are acting as reducing agents, whilst the copper oxide and ferric oxide are behaving as oxidizing agents.

Extended Definition of Oxidation and Reduction. If we denote by $\overline{O}$ the oxygen provided by an oxidizing agent, then the following reaction is clearly an oxidation reaction—

$$2FeO + \overline{O} = Fe_2O_3$$

This addition of oxygen to ferrous oxide involves an increase in the valency of iron from two to three to form ferric oxide. When these two oxides are dissolved in acids, they form the corresponding ferrous and ferric salts, reactions which do not involve any oxidation or reduction. Thus—

$$FeO + H_2SO_4 = FeSO_4 + H_2O$$

ferrous sulphate

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O$$

ferric sulphate

The conversion of a ferrous salt to a ferric salt is consequently rightly regarded also as an oxidation reaction—

$$FeSO_4 + \overline{O} \rightarrow Fe_2(SO_4)_3$$

But ferrous sulphate is composed of ferrous ions (Fe^{++}) and sulphate ions (SO_4^{--}), whilst ferric sulphate is composed of ferric ions (Fe^{+++}) and the same sulphate ions, so that this reaction may also be written—

$$Fe^{++} + \text{Sulphate ions} + \overline{O} \rightarrow Fe^{+++} + \text{Sulphate ions}$$

or even more simply by— $Fe^{++} \rightarrow Fe^{+++}$

Thus the oxidation of a ferrous to a ferric salt involves the conversion of a ferrous ion to a ferric ion, and this process clearly involves the removal of one orbital electron.

The extended definition of oxidation and reduction may therefore be stated as follows—

Oxidation involves an increase in the positive charge of the ion

$$Fe^{++} \rightarrow Fe^{+++} \qquad \underset{\text{stannous}}{Sn^{++}} \rightarrow \underset{\text{stannic}}{Sn^{++++}}$$

or, conversely, a decrease in the negative charge of the ion,

$$\underset{\text{manganate}}{(MnO_4)^{--}} \rightarrow \underset{\text{permanganate}}{(MnO_4)^{-}}$$

It also includes the simpler process of increasing the oxygen content of the molecule—

$$\underset{\text{sulphurous acid}}{H_2SO_3} \rightarrow \underset{\text{sulphuric acid}}{H_2SO_4}$$

Reduction involves a decrease in the positive charge of the ion or conversely an increase in the negative charge of the ion—

$$\underset{\text{cupric}}{Cu^{++}} \rightarrow \underset{\text{cuprous}}{Cu^{+}} \rightarrow \underset{\text{copper}}{Cu}$$

$$\underset{\text{iodine}}{I_2} \rightarrow \underset{\text{iodide}}{2I^{-}}$$

together with the processes involving a reduction in the oxygen content of the molecule—

$$\underset{\text{arsenic acid}}{H_3AsO_4} \rightarrow \underset{\text{arsenious acid}}{H_3AsO_3}$$

$$\underset{\text{sulphuric acid}}{H_2SO_4} \rightarrow \underset{\text{sulphuretted hydrogen}}{H_2S}$$

The principal oxidizing agents include oxygen, oxides of the less reactive metals (e.g. CuO), most peroxides and superoxides, most oxygen-containing compounds (nitrates, chlorates, dichromates, permanganates, persulphates, nitric acid, aqua regia, etc.), and solutions of iodine in potassium iodide. The soluble potassium permanganate, potassium dichromate, and solution of iodine in potassium iodide are particularly valuable in the volumetric methods of analysis involving oxidation-reduction reactions in solution.

The principal reducing agents include hydrogen, particularly in the nascent state (*see p.* 393), carbon monoxide and most lower oxides, various metallic salts in their lower valency state (e.g. stannous and ferrous salts), sulphuretted hydrogen, ammonia, and solutions of hydriodic acid and of arsenious oxide.

Of these, nascent hydrogen, stannous chloride, hydriodic acid and arsenious acid are used extensively as reducing agents in volumetric analysis.

Uses of Oxygen. Oxygen is supplied to industry under high compression (about 2000 lb/in.^{2} at 70°F) in steel cylinders painted black and containing usually 110 or 220 ft^3 of gas or as a liquid in large double-walled tanks of steel with a high vacuum between the walls. Its most important use is in the oxy-hydrogen and oxy-acetylene torches for cutting and welding steel. When acetylene gas burns with oxygen in a blowpipe, a temperature of about 2500°C is obtained, and this flame is used in welding metals, and also, when supplemented by a fierce jet of oxygen, in cutting through steel plates (even under water). The oxy-hydrogen flame is used principally in working platinum and silica, and is slightly more effective for this purpose than the oxy-coal-gas flame.

Oxygen is also used in hospitals and in aviation to assist respiration, and in the liquid state when mixed with powdered carbon and oil it is sometimes used as a blasting explosive.

A much wider use of oxygen in industry is however now developing. The increased efficiency of the modern plants for obtaining oxygen from the air is gradually leading to the use of oxygen or oxygen-enriched air in many commercial processes based on ordinary air as an oxidizing medium. Examples include the use of oxygen in the production of iron and steels (blast furnaces, open-hearth furnaces, etc.), in the underground gasification of coal, (a development still in its infancy) and in the generation of synthesis gas ($CO + H_2$) from methane (CH_4).

ACIDS, BASES AND SALTS

The terms *acid* and *base* were first applied to those substances which react together to form salts, usually together with water. Certain specific properties possessed by acids were later noted; for instance, they possessed a sharp or sour taste, and were able to turn blue litmus red, and to cause effervescence when added to chalk. Bases (or alkalis) were merely regarded as those compounds which could destroy or even reverse the effects caused by acids.

Lavoisier was the first to suggest a theory of acids. He noted that the oxides of such elements as carbon, sulphur, or nitrogen formed with water the corresponding carbonic, sulphuric and nitric acids. He was thus led to the theory that all acids contained oxygen. The name "oxygen," derived from the Greek which means "acid producer," was in fact given to the gas by Lavoisier.

Although this theory was generally accepted at the time, it had several weak points. It implied that hydrochloric acid contained oxygen, and hence that chlorine must be an oxide, since chlorine and hydrogen react together to form hydrochloric acid. The discovery of other halogen

acids (HBr and HI), and of the close similarity in properties of the parent halogens, all exposed the weakness of this theory.

Later it became apparent that one element was in fact present in all the compounds then regarded as acids, but that this element was hydrogen and not oxygen. Davy recognized hydrogen as the essential element in an acid, and later Liebig defined an acid as a compound containing hydrogen which could be replaced by a metal. Bases were still regarded as substances which could react with acids to form salts. The later development of the electrolytic dissociation theory as a result of the work of Ostwald and Arrhenius, resulted in the present-day generally accepted theory of an acid as a substance which produces hydrogen ions as the only positive ions in aqueous solution. Similarly basic properties are associated with the ability to produce hydroxyl ions in solution, and the neutralization of an acid by a base (or alkali) to form a salt is represented as—

$$\begin{array}{ccccccc} \text{Acid} & + & \text{Base} & = & \text{Salt} & + & \text{Water} \\ (H^+ + Cl^-) & + & (Na^+ + OH^-) & = & (Na^+ + Cl^-) & + & H_2O \end{array}$$

and involves the neutralization of the hydrogen ion by the hydroxyl ion to form neutral water.

This discussion of acids and bases would not however be complete if mention were not made of the extended definition of acids and bases embodied in the Lowry-Brönsted theory. Briefly, they regard acids and bases as complementary, in much the same way that oxidation and reduction are related, and define an acid as a species which has a tendency to lose a proton, and a base as a species which has a tendency to gain a proton—

$$\text{Acid} \rightleftharpoons \text{Base} + H^+$$

In non-aqueous solvents, in which no evidence of ionization may be detected, typical acid-base reactions do nevertheless occur. These reactions are depicted by the scheme—

$$(\text{Acid})_1 + (\text{Base})_2 \rightleftharpoons (\text{Base})_1 + (\text{Acid})_2$$

Typical acids on this theory include those neutral molecules HCl, HNO_3, etc., which are acids on the dissociation theory, but also included are such ions as HSO_4^-, HCO_3^-, NH_4^+. Similarly, bases include the metallic hydroxides, NH_3, and anions of weak acids, CH_3COO^-, etc. The electrolytic theory of acids and bases is however adequate for the subject-matter presented in this book.

An *acid* is defined as a compound which ionizes in water to produce hydrogen ions as the *only* positive ion, e.g. HCl, H_2SO_4, HNO_3, but not $NaHSO_4$ nor other compounds which would produce other positive ions besides the hydrogen ion. A strong acid is one which is completely or

almost completely ionized in solution; a weak acid as one which is only slightly ionized in solution.

A *base* is defined as a compound which will react with an acid to form a salt, usually together with water—

$$\text{BASE} + \text{ACID} = \text{SALT} + \text{WATER}$$

The term is applied to the hydroxides and oxides of the metals, but when the hydroxide is appreciably soluble in water it is also called an *alkali*. For example, potassium and sodium hydroxides are both bases and alkalis; copper hydroxide, magnesium oxide, etc., are simply bases. The alkalis ionize in aqueous solution to form hydroxyl ions.

A *salt* is the substance which results when an acid is treated with an alkali, in accordance with the above general equation. Salts which still contain hydrogen replaceable by a metal are known as *acid salts* or *hydrogen salts*, e.g. $NaHSO_4$ known variously as sodium hydrogen (acid or bi-) sulphate. A *basic salt* is one which still contains free base capable of reacting with an acid, thus basic copper sulphate may have the formula $CuSO_4 . Cu(OH)_2$. In the solid state, such a basic salt consists of Cu^{++} ions together with OH^- and SO_4^{--} ions.

CHAPTER 18

WATER

Introduction. Although water has the simple molecular formula H_2O, it is nevertheless the most precious of all fluids, in many respects the most important chemical compound and, paradoxically, in some respects one of the most dangerous compounds. It occurs as rain, hail and snow, in bulk in the streams, rivers and oceans; it is consumed as a drink, both in its natural state and as a beverage. Less familiar are its effects throughout the ages in the weathering and disintegration of rocks to produce soil, the latter when cultivated providing so much of the foodstuffs essential to life. The enormous energy possibilities of water and the dependence of modern civilization upon hydro-electric power and steam power are nowadays well understood. Water also plays an important role in most chemical reactions either as one of the reacting compounds, or as a solvent, or sometimes (when present often only in very small concentrations) as an essential catalyst. On the debit side, the enormous wastage of metals, particularly of the ferrous metals, by atmospheric corrosion (rusting, etc.) is caused mainly by atmospheric oxidation in presence of water or moisture. The rotting of materials, fabrics, etc., the putrification of refuse, the contraction of various diseases (e.g. malaria, typhoid, etc.) are all dependent in one way or another on the presence of water. Some of these varied modes of action of water will be discussed elsewhere in this book, but in this chapter we shall concern ourselves with water in the general sense, its composition, physical and chemical properties.

THE COMPOSITION OF WATER

Qualitative. That water is composed only of hydrogen and oxygen may be shown both by synthesizing water from these two elements and also by showing that only these two elements are produced when water is decomposed.

Synthesis. (*a*) When dry hydrogen is allowed to burn in air or oxygen as in the experiment described on p. 369, a liquid product is obtained which has the same physical and chemical properties as water, and is in fact water. A quick test for water is to add a little to some anhydrous copper sulphate. In the presence of water copper sulphate immediately changes colour from white to pale blue, due to hydration of the copper ion—

$$Cu^{++} + 4H_2O = Cu(H_2O)_4{}^{++}$$

the overall reaction being usually represented as—

$$CuSO_4 + 5H_2O = CuSO_4 . 5H_2O$$

copper sulphate penta-hydrate

This reaction by itself, however, would be insufficient adequately to identify the liquid as water; other tests must also be carried out in confirmation.

(*b*) The direct combination of hydrogen and oxygen to form water may also be carried out by exploding the dry gases together in a eudiometer, or by passing the mixed gases over a suitable catalyst such as platinum black (a very finely divided form of platinum) at ordinary temperatures. In the eudiometer experiment, described below, the reaction occurs as a result of the local high temperature produced by passing an electric spark through a small portion of the gas. The reaction so initiated then occurs explosively as a result of a chain reaction (*see* p. 370).

$$2H_2 + O_2 = 2H_2O$$

(*c*) Water is also produced by the reducing action of gaseous hydrogen on the oxides of the less reactive metals, such as copper oxide, CuO, and the oxides of mercury, lead, etc.—

$$CuO + H_2 = Cu + H_2O$$

This reaction may be carried out by passing dry hydrogen over the heated copper oxide contained in a hard glass tube as in the diagram shown on p. 400. Reactions (*a*), (*b*) and (*c*) each show the presence of either or both hydrogen and oxygen in water.

Decomposition. (*a*) The decomposition of water into hydrogen and an oxide—

$$\text{Water} + \text{Element} \rightarrow \text{Hydrogen} + \text{Oxide (or Hydroxide)}$$

may be produced by the action, under suitable conditions, of the more reactive metals, and of certain of the non-metals, with water. Examples of these reactions include—

(i) $$2Na + 2H_2O = 2NaOH + H_2\uparrow$$

This reaction occurs vigorously at ordinary temperatures, but by plunging a little sodium, wrapped in wire gauze, beneath the surface of the water, the hydrogen may be collected and identified.

(ii) $$Mg + H_2O = MgO + H_2$$

In this case, steam is passed over strongly heated magnesium ribbon contained in a hard glass tube. The above reaction occurs when the

magnesium burns and the hydrogen liberated may be collected over water in the usual way (*see* Fig. 152).

(iii) $$C + H_2O = CO + H_2$$

This reaction is the important *water-gas* reaction, and occurs when steam is passed over, or through, a bed of white hot coke. The carbon monoxide may be removed by ammoniacal cuprous chloride solution as described on p. 464.

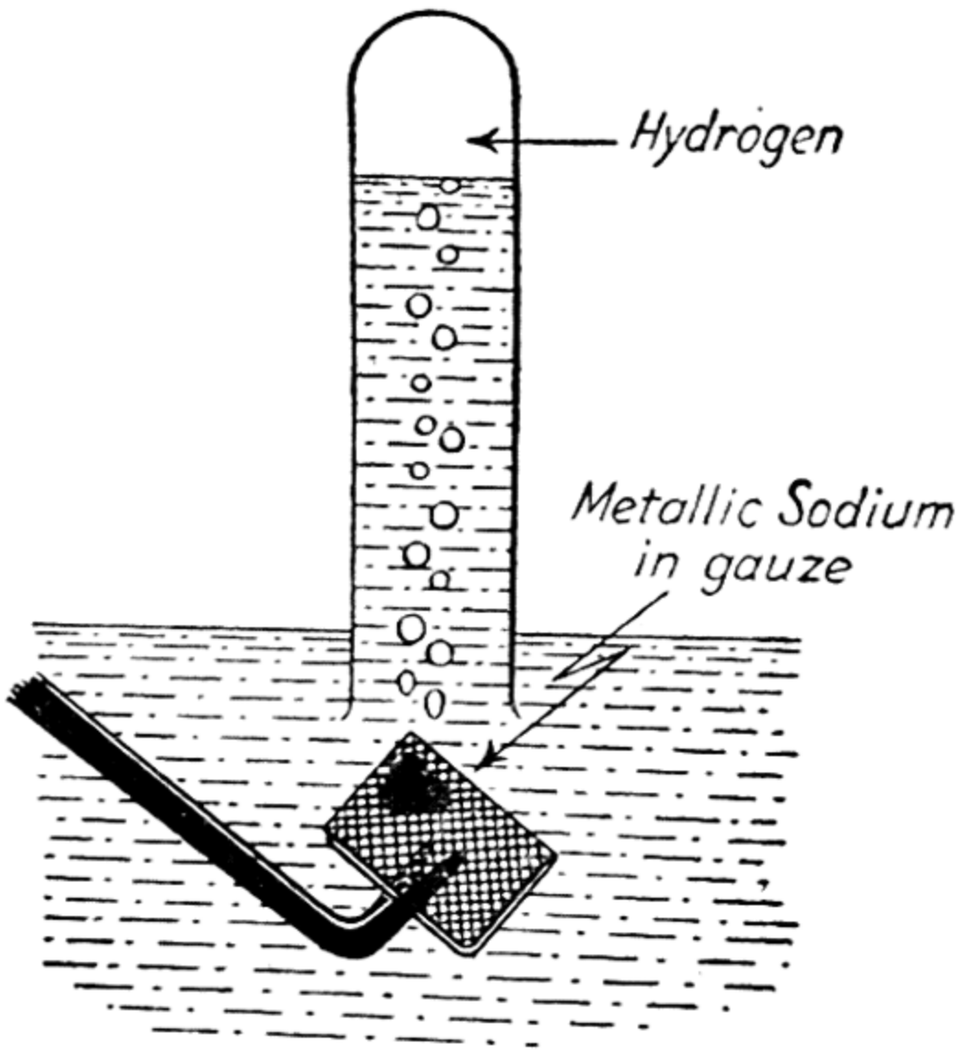


FIG. 143. Action of Water on Sodium

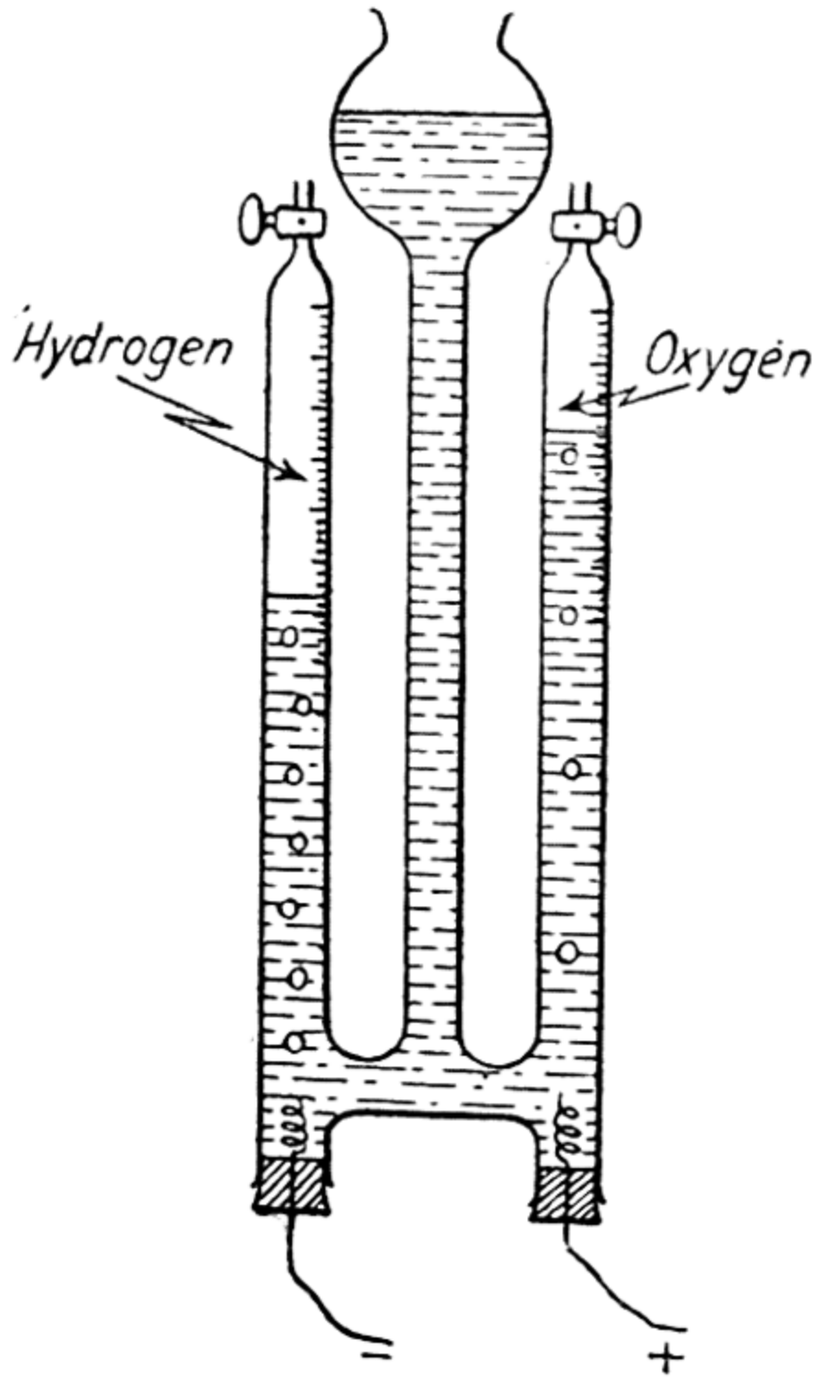


FIG. 144. Hofmann Voltameter

(*b*) The decomposition of water by thermal dissociation requires an extremely high temperature, so that this method is of little practical value for the purpose of determining the composition of water. Far simpler is the electrolysis of water using platinum electrodes, as in the Hofmann voltameter. Since water is a poor electrical conductor, some sulphuric acid is usually added, so that the electrolyte is dilute sulphuric acid and not water. Oxygen is liberated at the positive electrode or anode, and hydrogen at the negative electrode or cathode.

Electrolyte—

$$H_2O = H^+ + OH^-$$
$$H_2SO_4 = 2H^+ + SO_4^{--}$$

Cathode Reaction—

$$H^+ \rightarrow H \rightarrow \underset{\text{hydrogen}}{H_2}$$

Anode Reactions: (*a*) discharge of $(OH)^-$ ions—

$$OH^- \rightarrow (OH) \qquad 4(OH) \rightarrow 2H_2O + O_2$$

(*b*) discharge of SO_4^{--} ions; $SO_4^{--} \rightarrow (SO_4)$, which is followed immediately by—

$$(SO_4) + H_2O \rightarrow H_2SO_4 + (O) \text{ and } 2(O) \rightarrow O_2$$

These reactions show that the sulphuric acid destroyed by the electrolysis is being continuously reformed by the secondary reactions at the anode, so that the actual amount of sulphuric acid present remains unchanged, a conclusion which may easily be verified by analysis.

The hydrogen and oxygen gases are thus seen to result essentially from the decomposition of water. The important point to note in this experiment is that twice as much hydrogen (by volume) collects in the cathode chamber as oxygen in the anode chamber.

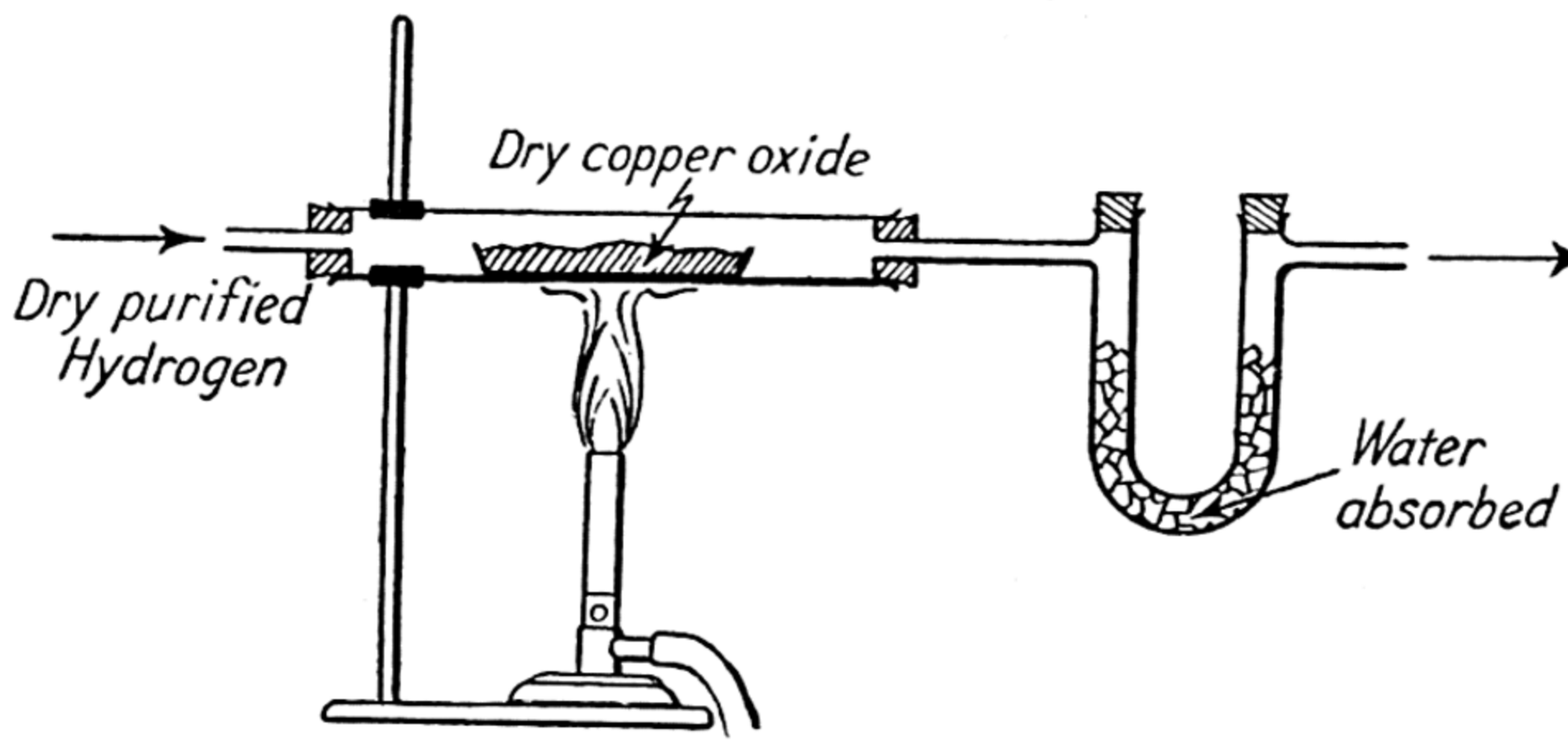


FIG. 145. Simple Laboratory Version of Dumas' Apparatus

The Composition of Water by Weight

The works of two investigators are of classical importance in connexion with the quantitative determination of the combining ratio of hydrogen and oxygen in water. The first of these by Dumas in 1843 may indeed be considered to inaugurate a period during which many atomic weights were determined accurately, whilst the second, by Morley in 1895, is still considered a model of such determinations and resulted in a value for the atomic weight of hydrogen which differs only very slightly from the present-day generally accepted value.

Dumas' Determination. The method adopted by Dumas was based on the reaction—

$$CuO + H_2 = Cu + H_2O$$

in which water is formed by the reducing action of hydrogen gas passed over heated copper oxide. A simplified laboratory version of the apparatus used is shown in Fig. 145. The water formed was carefully collected and

weighed. The weight of oxygen contained in this weight of water was found by weighing the copper oxide before and after the reduction, the difference giving directly the weight of oxygen. The weight of hydrogen in the water was then found indirectly by subtracting this value from the weight of water formed.

The hydrogen prepared by the action of zinc on previously boiled dilute sulphuric acid was purified by passing successively through seven U-tubes containing—

(*a*) pieces of glass moistened with lead nitrate to remove sulphuretted hydrogen, H_2S,

(*b*) solution of silver sulphate to remove arsine, AsH_3,

(*c*) three tubes of caustic potash to remove sulphur dioxide, carbon dioxide and nitrogen oxides, and

(*d*) phosphorus pentoxide to dry the gas.

In order to confirm that the purified hydrogen was completely dry at this stage, it was next passed through a U-tube containing phosphorus pentoxide which was weighed before and after each experiment. If no change in weight occurred it followed that the hydrogen had been completely dried.

The reaction—

$$CuO + H_2 = Cu + H_2O$$

was then carried out by passing the dry purified hydrogen over dry copper oxide contained in a hard glass bulb, which was heated externally during the experiment by a spirit lamp. This bulb was weighed before and after each experiment, the difference in weight giving the weight of oxygen which had been removed as water. Each experiment lasted some 10–12 hours.

The water mostly condensed in a second smaller bulb, whilst the remainder was absorbed from the excess of hydrogen, as the latter passed out of the apparatus, by passing through—

(i) a U-tube containing solid potassium hydroxide, KOH,

(ii) two U-tubes containing phosphorus pentoxide, P_2O_5, the first of which was cooled throughout the experiment in ice,

(iii) another U-tube containing P_2O_5 and finally through a concentrated H_2SO_4 bubbler which protected the apparatus from the back diffusion of moisture from the outside atmosphere into the apparatus. The bulb and U-tubes (i) and (ii) were carefully weighed before and after the experiment. The net increase in weight of these gave the weight of water formed in the experiment.

Result. The average of nineteen experiments gave the following results: 7·98 parts by weight of oxygen combine with 1·00 part by weight of

hydrogen to form water, or 8·00 parts of oxygen combine with 1·002 parts by weight of hydrogen.

The principal sources of error in Dumas' estimation appear to be—

(*a*) As the reduced copper cools, it adsorbs or absorbs some of the hydrogen gas, thereby increasing slightly in weight.

(*b*) The liberation of hydrogen from sulphuric acid results in some of the dissolved air being carried away with the hydrogen. The oxygen present in this air is ultimately converted by the hydrogen and copper into water, whilst the nitrogen also present in this air may contaminate the copper oxide.

Morley's Determination of the Composition of Water by Weight. Morley's method was based on the direct combination of carefully purified and dried hydrogen and oxygen to form water—

$$2H_2 + O_2 = 2H_2O$$

Unlike Dumas, in addition to weighing the oxygen and water, he also weighed the hydrogen, and the accuracy of his work is immediately revealed by the very close agreement between the weight of water formed and the sum of the weights of hydrogen and oxygen used.

Preparation and Weighing of the Pure Dry Hydrogen. Hydrogen prepared by the electrolysis of dilute sulphuric acid was purified by passing through strong potassium hydroxide solution (to remove any acid spray), over red-hot copper (to remove the slight oxygen impurity), and then thoroughly dried by passing successively through three long tubes containing, respectively, glass beads moistened with concentrated potassium hydroxide solution, glass beads moistened with concentrated sulphuric acid, and finally glass wool and phosphorus pentoxide. The dry pure hydrogen was then absorbed in palladium, and weighed.

Preparation and Weighing of the Pure Dry Oxygen. The oxygen was prepared by heating potassium chlorate, and then dried and purified by passing through three long tubes as in the case of hydrogen. The oxygen was then collected in previously evacuated large glass globes, and weighed.

Morley's apparatus is shown in Fig. 146. This was first evacuated and weighed. The gases, hydrogen and oxygen were then admitted through the two side arms containing phosphorus pentoxide into the reaction chamber. Sparks were then passed across the platinum points so that ignition of the hydrogen occurred to form water. The rate of entry of the hydrogen and oxygen at their respective jets was regulated during each experiment to ensure a continous formation of water. This water condensed and collected in the lower part *A* of the middle chamber. At the end of an experiment, the apparatus was immersed in a freezing mixture and the residual gases (containing both hydrogen and oxygen) pumped off through the P_2O_5 tubes (which retained any moisture) and analysed.

The weights of hydrogen and oxygen so obtained were added to the appropriate weights of hydrogen and oxygen which remained in the palladium and oxygen reservoirs. The weight of water formed was found directly by finding the increase in weight of the reaction vessel.

As mentioned above, the very close agreement between the weights of hydrogen and oxygen used and the weight of water formed reveals the

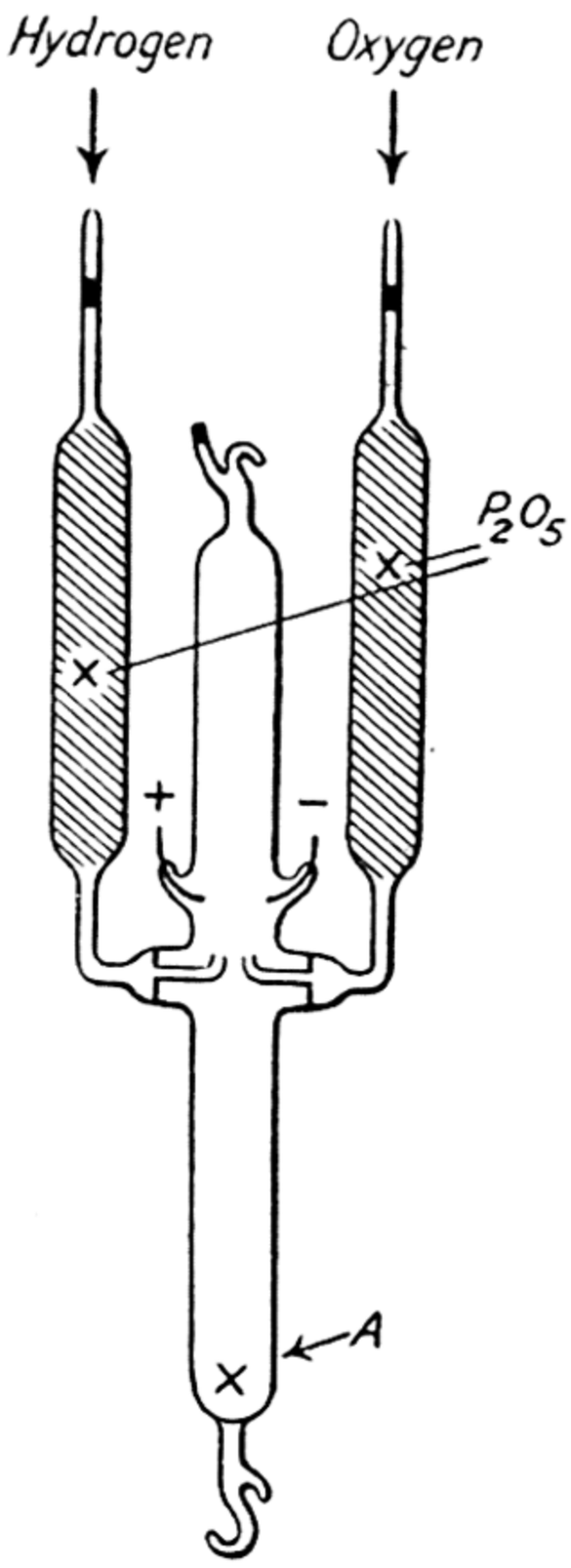


FIG. 146. Morley's Apparatus

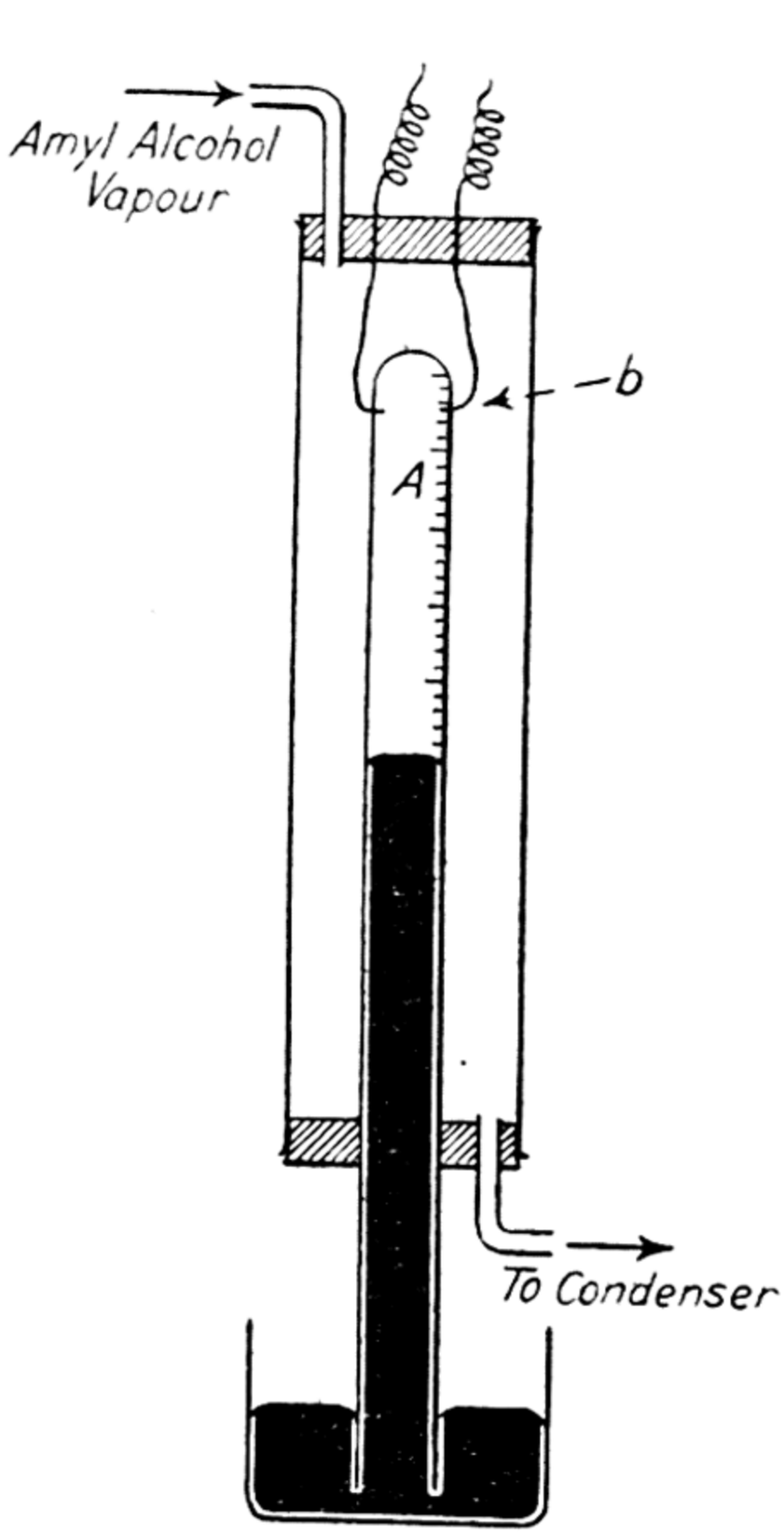


FIG. 147. Eudiometer (Composition of Water by Volume)

thoroughness and accuracy of Morley's determination. As a mean of twelve experiments, he found that 8·00 parts of oxygen combined with 1·00762 parts of hydrogen, a value slightly greater than that found by Dumas, viz. 8:1·002.

Composition of Water by Volume

The simplest way of determining the combining ratio by volume of hydrogen and oxygen to form water is to use a eudiometer, a simple form of which is shown in the accompanying diagram. A known volume of oxygen and a known volume of hydrogen (in excess) is contained over mercury in the space *A*. The amyl alcohol vapour jacket ensures that the

water formed on passing sparks across *b* remains in the vapour state. The contraction in volume after the explosion is noted, and also the volume of hydrogen which remains when the water is later condensed. These results show that the volumes of hydrogen and oxygen used, and the volume of steam formed, are almost exactly represented by—

$$2 \text{ volumes of } H_2 + 1 \text{ volume of } O_2 \rightarrow 2 \text{ volumes of steam}$$

Applying Avogadro's hypothesis, (that equal volumes of all gases under the same conditions of temperature and pressure contain equal numbers of molecules), it follows that—

$$2H_2 + O_2 = 2H_xO_y$$

so that x must equal two and y one to give the molecular formula of water as H_2O.

The method of calculating such an answer from the experimental results is best exemplified by making the calculation.

20 ml of oxygen and 60 ml of hydrogen after sparking contracted to 60 ml (temperature of jacket $> 100°C$). On cooling (to condense the water vapour) the volume further contracted to 20 ml. All volumes have been corrected to S.T.P. conditions.

Calculation

Since excess of hydrogen was used, the residual volume (i.e. 20 ml) at the end of the experiment must be hydrogen. Hence, volume of hydrogen used during the experiment is 40 ml.

The volume of oxygen used is equal to the volume of oxygen initially present, namely 20 ml.

The volume of steam produced is found by subtracting the volume of excess hydrogen from the total volume of gases remaining after passing the sparks, i.e. 60–20 ml, that is, 40 ml. It may alternatively be found by observing the contraction when the temperature is reduced from above 100°C to below 100°C.

These results show that—

$$40 \text{ ml } H_2 + 20 \text{ ml } O_2 \rightarrow 40 \text{ ml } H_2O \text{ (vapour)}$$

If we let "1 volume" represent 20 ml, then—

$$2 \text{ vols } H_2 + 1 \text{ vol } O_2 \rightarrow 2 \text{ vols } H_2O$$

whence, as above, the formula of water is H_2O.

The most accurate determination of the combining ratio (by volume) of hydrogen and oxygen to form water is that of Burt and Edgar (1916), and the student is referred to such text-books as *General and Inorganic Chemistry* by Partington for a description of the experiments. As a result of some fifty-nine determinations, they found that—

$$1 \text{ volume of hydrogen} + 2{\cdot}00288 \text{ volumes of oxygen} \rightarrow \text{water}$$

This slight departure from the simple 1:2 ratio to be expected from the Gay-Lussac Law (when gases combine together they do so in volumes which are simply related) is now known to be due to the imperfect nature

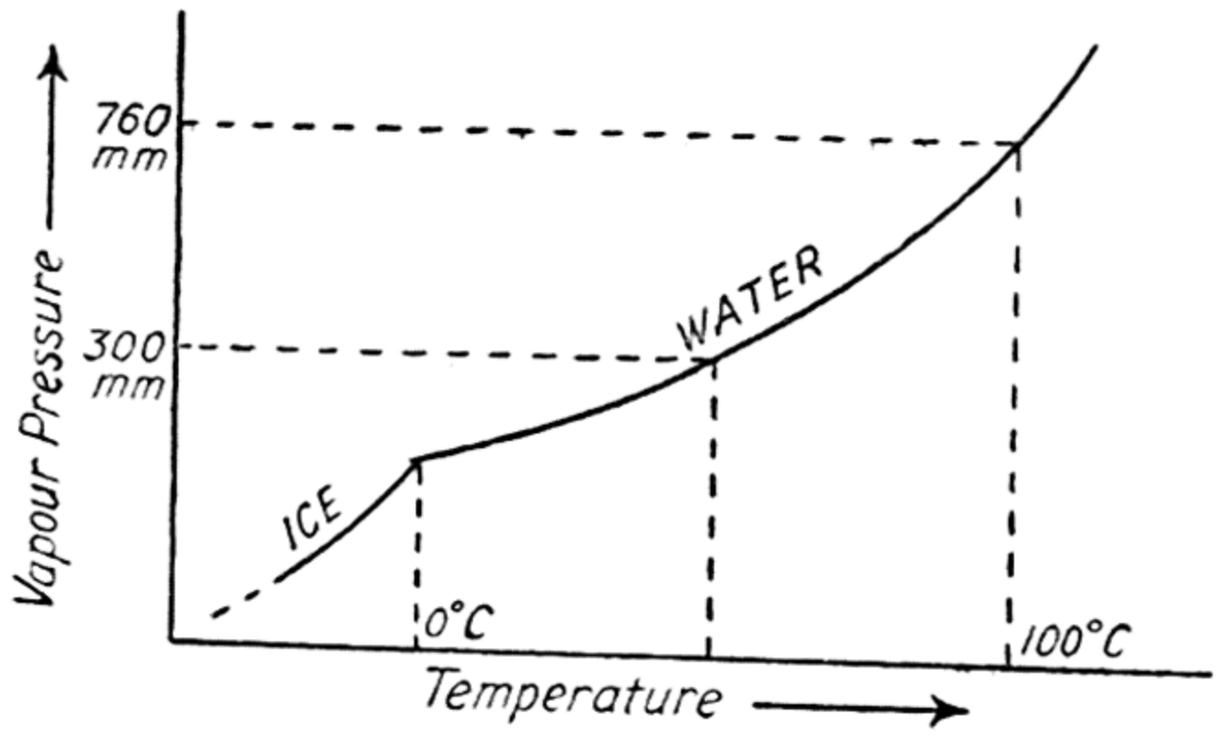


FIG. 148. Vapour Pressure Curve for Water

of the gases which in fact do not rigidly obey the perfect gas laws (Boyle's, Charles's, Dalton's, etc.).

Physical Properties. The statement that water boils at 100°C and freezes at 0°C is true only when the pressure on the water is the standard atmospheric pressure of 760 mm Hg. A liquid boils when its vapour pressure is equal to the external pressure; in air, this will be the atmospheric pressure. Similarly water freezes when its vapour pressure equals the vapour pressure of ice. The above diagram (Fig. 148) shows the way in which the vapour pressure of water varies with temperature; at 760 mm Hg pressure, water boils at 100°C, but at 300 mm pressure, for example, it will boil at 75·9°C.

The density of water varies with temperature as shown in Fig. 149. A decrease in volume occurs when ice melts, and the volume of the water produced continues to decrease with further increase in temperature until at 4°C the water reaches its maximum density. Above this temperature the volume begins to increase again, in agreement with the normal behaviour of a liquid. The behaviour below 4°C is now known to result from the relatively open arrangement of the water molecules in the solid ice structure. The work of Bernal and Fowler has shown that in ice the water molecules have a three-dimensional tetrahedral arrangement, based on a tetrahedral arrangement of the bonds from each water molecule. The latter is regarded essentially as an oxygen

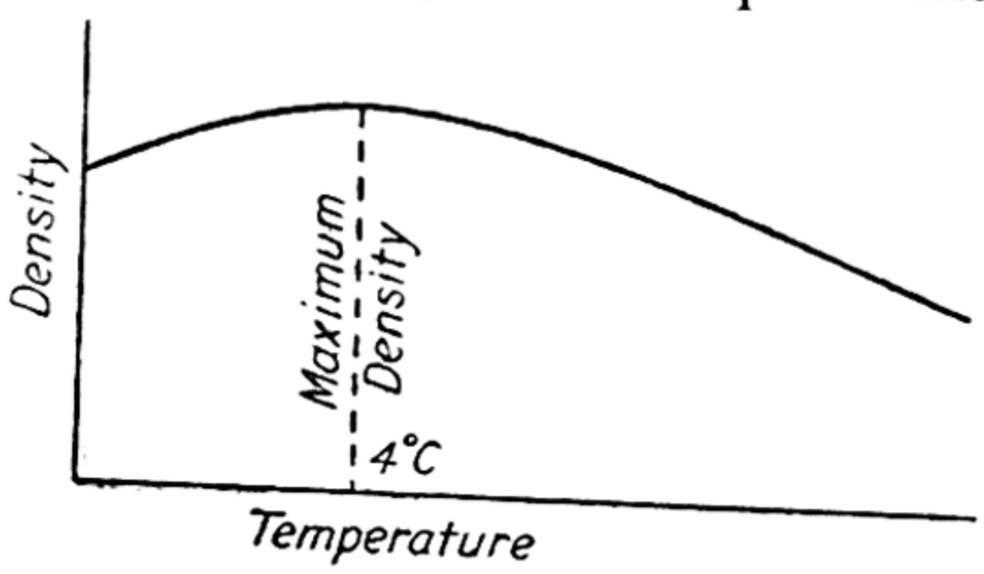
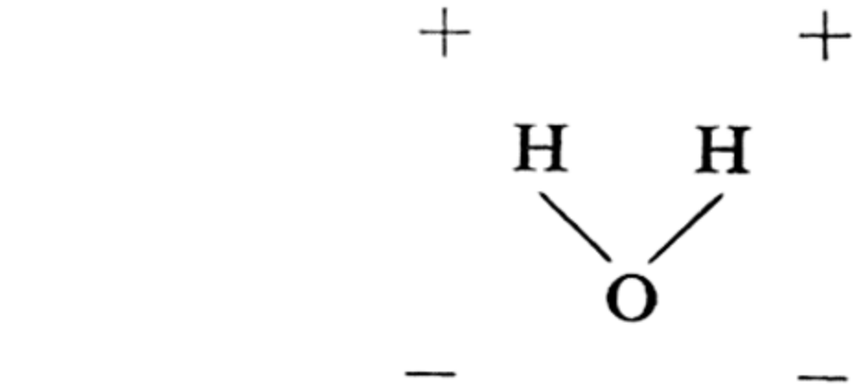


FIG. 149. Variation of the Density of Water with Temperature

ion in which are embedded two hydrogen ions (*see* adjoining sketch) so that the molecule as a whole has a tetrahedral charge distribution, two



positive and two negative, each approximating in value to $\frac{1}{2}e$. When ice melts, this open structure mainly, but not completely, collapses and a

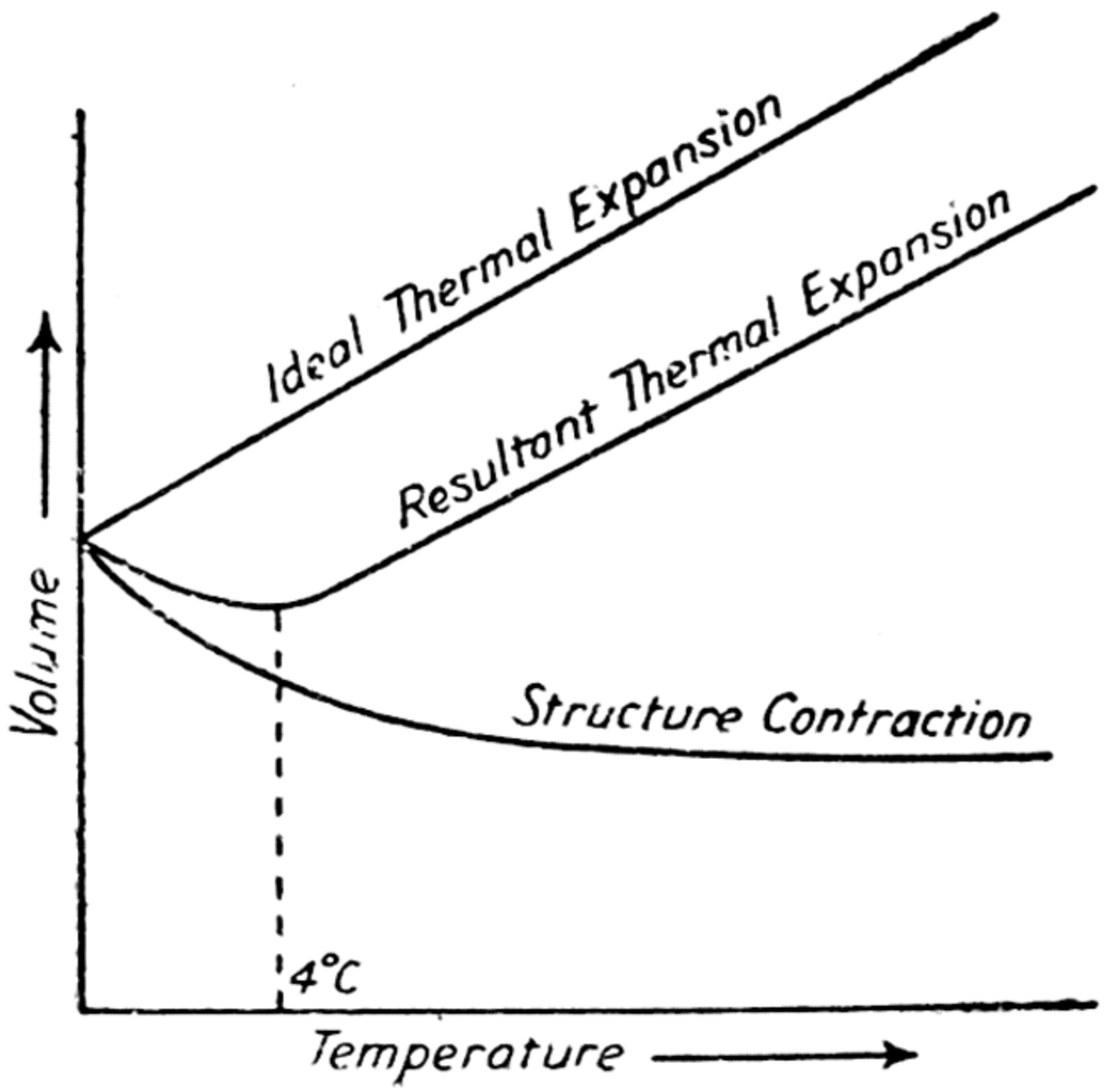
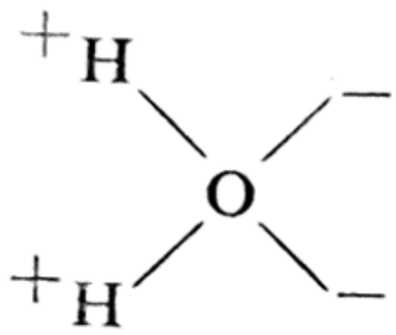


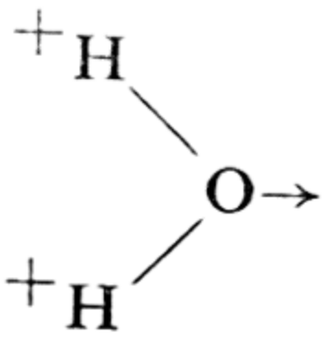
FIG. 150. Effect of Structure on the Expansion of Water

contraction in volume and increase in density occurs. Water at 0°C still retains an appreciable tendency to associate with other water molecules, and probably consists of loose complexes of two, three, or even more molecules. With increase in temperature and consequent increase in the energy content of the molecule, this random structure of water gradually breaks up, producing as in the case of the melting of ice a further contraction in volume. The accompanying diagram (Fig. 150) shows qualitatively how this contraction in volume is compensated by the normal expansion of a liquid with rise in temperature, and explains why water reaches its maximum density at a temperature which is higher than the melting point, i.e. at 4°C. In crystalline hydrates, discussed below, the molecules

of water of crystallization show the same tetrahedral arrangement of bonds as in ice—



and also an arrangement in which the bonds are planar—



The expansion of ice on melting and of water up to 4°C plays an important role in nature. As water is cooled below 4°C, the colder water, since it is less dense, rises to the surface and ice eventually forms as a surface layer. If the reverse were the case, and the density increased continuously (with a further increase on freezing) then the freezing of fresh water lakes, etc., would occur initially at the lowest point and gradually spread upwards. This solid block of ice might well persist throughout a normal summer, since it would be thermally insulated by the upper layer of water from the warmth of the sun's rays. Marine fish and vegetable life could hardly survive under these conditions, and in addition the existence of these solid blocks of ice might well induce profound climatic changes which would affect civilization as a whole.

The student will have encountered the terms millilitre (ml) and cubic centimetre (c.c.) as units of volume. The c.c. is the volume occupied by one gramme of pure water at 4°C, and was originally thought to be the same as the ml, which is one-thousandth part of the volume of the litre, a standard of volume kept in Paris. On reinvestigating the litre standard in 1910, it was found that the water filling it at 4°C weighed slightly more than 1000 g, namely, 1000·027 g. The ml was thus found to be equal to 1·000027 c.c. In modern volumetric practice the unit of volume is the ml, but for most practical purposes the difference between the two units is so small as to be entirely negligible.

Water plays a very important role as an ionizing solvent. It will dissolve most substances which are themselves essentially electrovalent or ionic, such as most salts, acids, alkalis, etc., but it will not dissolve the other very large class of compound which are essentially covalent, such as the majority of organic compounds, of which petrol, benzene, paraffin wax, butter, lard, etc., may be quoted as examples. The phrase, "like dissolves like" is a very useful working rule. Water is itself an electrolyte although, it must be added, a very poor one. The specific conductivity of pure water at

25°C is only $0{\cdot}04 \times 10^{-6}$ mhos, or in other words the electrical resistance of one c.c. of water between two electrodes each one cm^2 in area is as high as $2{\cdot}5 \times 10^7$ ohms. As an ionizing solvent, however, water occupies almost an unique position. Other ionizing solvents, such as liquid ammonia, liquid sulphur dioxide, and anhydrous hydrogen fluoride are also known, but these are mostly of theoretical interest and play no important part in our everyday lives.

The purification of water for domestic and industrial purposes probably plays the biggest part in the chemistry of water. The discussion of this very important topic is postponed, however, to Chapter 20.

Chemical Properties. It will help the student to understand the chemistry of water if we first discuss briefly the ways in which it may react. In the molecule, H_2O, each atom has acquired its full complement of electrons by covalency linkages—

$$H \times \dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{O}}} \times H$$

that is $H—O—H$ or H_2O

and the molecule is quite stable. We must therefore look to the other reactant for the primary cause of any resultant chemical reactivity. If this reactant does not possess the inert-gas electronic configuration, then, under suitable conditions, it may remedy this deficiency either by disrupting the water molecule (as in the reaction of the metals with water) or by direct combination with water molecules (as in the crystalline hydrates). If the reactant can be oxidized, then under appropriate conditions the water will act as an oxidizing agent and hydrogen will be liberated (as in the burning of magnesium in steam). Finally, some reactions, such as the hydrolysis of salts, depend upon the small degree of ionization of water to produce hydrogen and hydroxyl ions, H^+ and $(OH)^-$.

$$H_2O \rightleftharpoons H^+ + (OH)^-$$

These four types of reactivity may be summarized—

(*a*) reaction of certain metals (and non-metals) with liquid water,
(*b*) reactions of certain other metals (and non-metals) with steam,
(*c*) hydrolysis reactions, and
(*d*) formation of hydrates, such as $CuSO_4 . 5H_2O$.

Reaction of Metals with Water

Potassium reacts violently with water, even when cold, to liberate hydrogen and form potassium hydroxide. The hydrogen liberated is ignited by the heat of the reaction and burns with the lilac flame characteristic of potassium.

The reaction $2K + 2H_2O = 2KOH + H_2$ results from the tendency of the potassium atom, with the electronic structure 2 . 8 . 8 . 1, to lose one electron and so acquire the inert-gas electronic structure of argon, viz. 2 . 8 . 8. Thus—

$$K \rightarrow e \rightarrow (H—O)^-—H = K^+(OH)^- + (H)$$

followed by

$$2(H) \rightarrow \underset{\text{hydrogen gas}}{H_2}$$

Sodium also reacts violently with water; the heat of the reaction is sufficient to melt the sodium (which moves rapidly over the surface of the water as a silvery ball) but insufficient to ignite the hydrogen, unless the motion of the sodium be restricted as for example by floating the sodium in water on a piece of blotting paper, or by using hot water. The hydrogen then burns with a yellow flame characteristic of sodium.

$$2Na + 2H_2O = 2NaOH + H_2$$

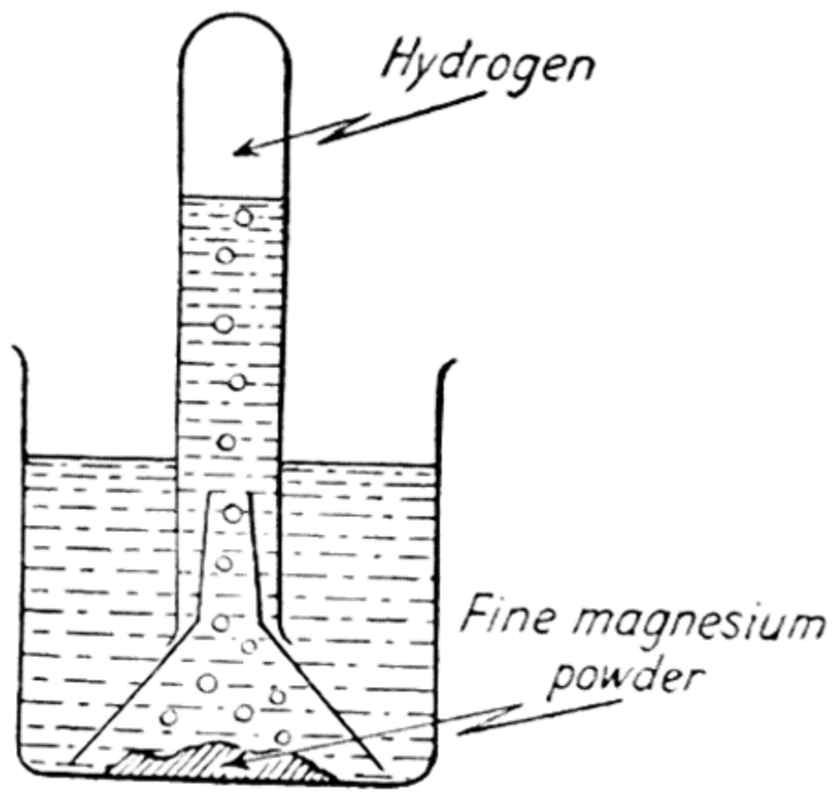


FIG. 151. Action of Water on Magnesium

Calcium, being heavier than water, sinks to the bottom and then reacts slowly. The reaction gradually slows up due to the formation of moderately soluble calcium hydroxide which tends to protect the calcium metal from further reaction with the water.

$$Ca + 2H_2O = Ca(OH)_2 + H_2$$

Barium reacts more readily with water since the resulting barium hydroxide is quite soluble, and so does not protect the metal from further reaction.

Magnesium. Very finely divided magnesium reacts very slowly with cold water, and slightly more rapidly on heating, as the experiment illustrated in Fig. 151 will show.

Reactions of the Metals with Steam

Magnesium. When magnesium is heated strongly in steam, it ignites and burns with its usual brilliant flame to form the oxide and liberate hydrogen—

$$Mg + \underset{\text{steam}}{H_2O} = MgO + H_2$$

It is probable that a very slight dissociation of the gaseous water molecules into free hydrogen atoms and hydroxyl radicals occurs

$$H_2O = H + OH$$

and that reaction takes place to form initially magnesium hydroxide which then decomposes at this temperature to form magnesium oxide

$$Mg + 2(OH) \rightarrow Mg(OH)_2$$

$$Mg(OH)_2 \rightarrow MgO + H_2O$$

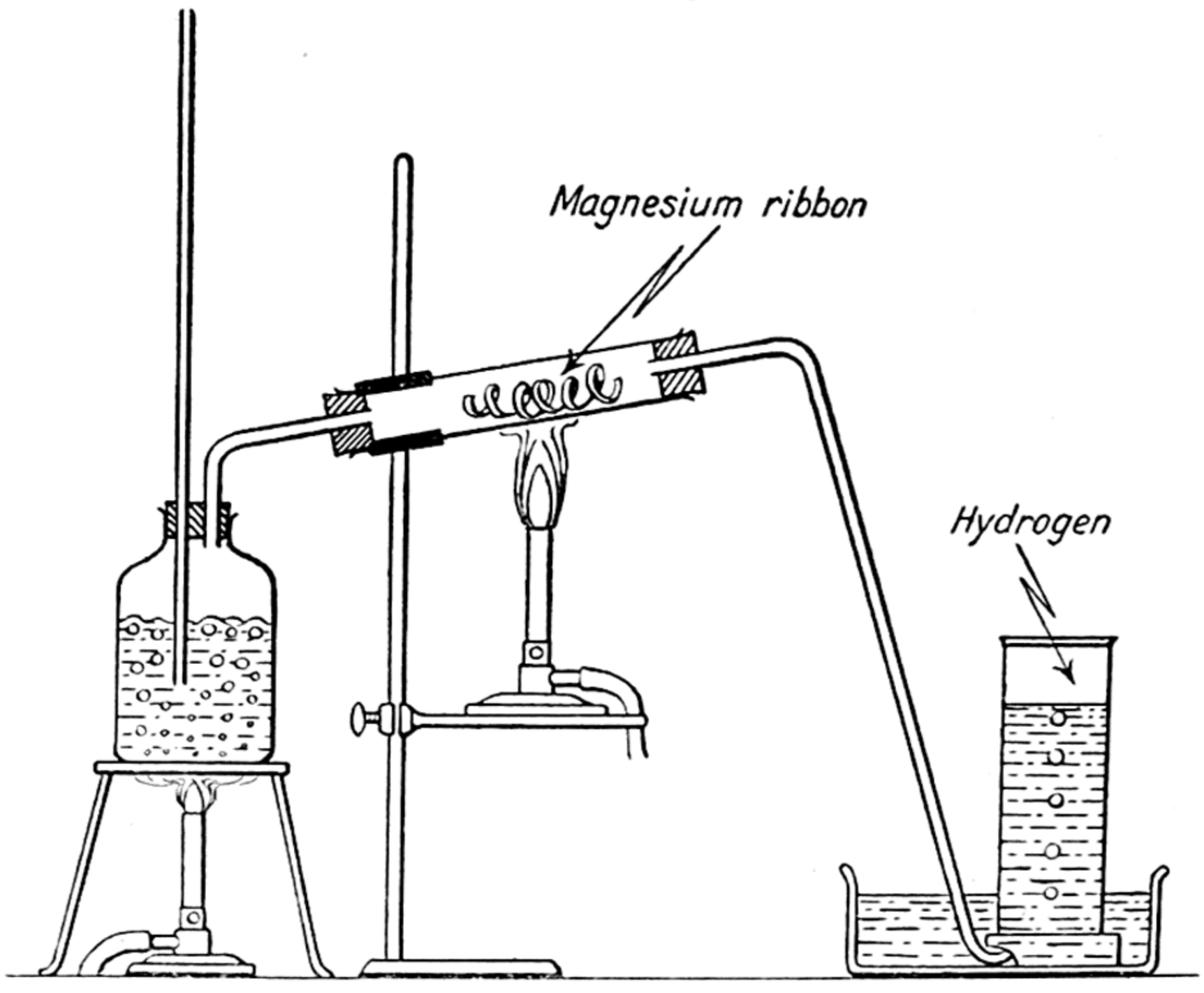


FIG. 152. Burning of Magnesium in Steam

Measurements of the absorption spectrum of water vapour at high temperatures show the presence of lines due to the OH radical, in agreement with the probable mechanism of the reaction suggested above.

Aluminium, apparently, does not react with water, but if the very adherent and impervious coating of oxide, Al_2O_3, is not allowed to form, for example, by immersing the aluminium in a solution of a mercuric salt for a short time, then reaction occurs readily both with water and with steam, to liberate hydrogen and form aluminium hydroxide (or oxide).

$$2Al + 3Hg(NO_3)_2 = 2Al(NO_3)_3 + 3Hg$$

$$\text{Aluminium} + \text{Mercury} \rightarrow \text{Aluminium amalgam}$$

Zinc will burn when heated strongly in steam to form the oxide and liberate hydrogen.

Iron requires superheated steam before reaction occurs to form ferroso-ferric oxide, Fe_3O_4. The student will recall that this reaction is reversible and is the basis of the Lane process for preparing reasonably pure hydrogen (99 per cent) on a commercial scale.

The metals below hydrogen in the electrochemical series (*see* p. 272) do not react with either water or with steam. It is probable that if oxidation could occur in the latter case, the hydrogen liberated would immediately reverse the process, and the net result would be no reaction. These remarks apply to such metals as copper, silver, platinum, gold, etc.

Reaction of Non-metals with Water

Chlorine. The solution in water reacts slightly to form hypochlorous acid and hydrochloric acid—

$$Cl_2 + H_2O = HCl + \underset{\text{hypochlorous acid}}{HClO}$$

In sunlight, the hypochlorous acid slowly decomposes and oxygen is liberated—

$$2HClO = 2HCl + O_2$$

Fluorine reacts vigorously with water to form hydrofluoric acid (H_2F_2) and oxygen, with no indication of any intermediate stage as in the case of chlorine. Sometimes, an unexplained inhibition occurs, and quantities of water may accumulate in the presence of fluorine until the reaction is suddenly initiated with explosive violence.

Carbon. When steam is passed through a bed of white hot coke, the "water gas" reaction occurs to form carbon monoxide and hydrogen—

$$C + H_2O = CO + H_2$$

Silicon shows a similar reactivity, but the reaction occurs more slowly—

$$Si + 2H_2O = \underset{\text{silica}}{SiO_2} + 2H_2$$

Hydrolysis Reactions

Hydrolysis is essentially the tendency for the reaction

$$\text{Base} + \text{Acid} = \text{Salt} + \text{Water}$$

to occur in the reverse direction, and is the reason for the slightly acidic or alkaline behaviour of solutions of certain salts. Thus salts of strong acids and weak bases give slightly acid solutions—

$$CuSO_4 + 2H_2O \rightleftharpoons \underset{\text{weak base}}{Cu(OH)_2} + \underset{\text{strong acid}}{H_2SO_4}$$

Conversely salts of weak acids and strong bases give alkaline solutions—

$$\underset{\text{strong base}}{Na_2CO} + 2H_2O = 2NaOH + \underset{\text{weak acid}}{H_2CO_3}$$

The resulting acidic or alkaline character of the solution is thus determined by the relative strengths of the acid and base which tend to form during the hydrolysis. Thus, sodium hydroxide is a strong base whilst carbonic acid is a very weak acid.

The term *hydrolysis* is also used to describe the reaction with water of certain compounds which are not salts. These compounds are essentially covalent compounds, and often react merely on exposure to the moisture of the atmosphere. Most of the examples of this type of hydrolysis are found in the chlorides of the non-metals and of certain metals, for example—

$$\underset{\substack{\text{phosphorus}\\\text{trichloride}}}{PCl_3} + 3H_2O = H_3PO_3 + 3HCl$$

$$\underset{\substack{\text{phosphorus}\\\text{pentachloride}}}{PCl_5} + H_2O = POCl_3 + 2HCl$$

$$\underset{\substack{\text{phosphorus}\\\text{oxychloride}}}{POCl_3} + 3H_2O = H_3PO_4 + 3HCl$$

$$\underset{\substack{\text{sulphuryl}\\\text{chloride}}}{SO_2Cl_2} + 2H_2O = H_2SO_4 + 2HCl$$

$$\underset{\substack{\text{stannic}\\\text{chloride}}}{SnCl_4} + 4H_2O = Sn(OH)_4 + 4HCl$$

$$\underset{\substack{\text{titanium}\\\text{chloride}}}{TiCl_4} + 4H_2O = Ti(OH)_4 + 4HCl$$

These compounds fume when exposed to air due to the liberation of hydrogen chloride gas, which combines with the moisture of the atmosphere to form very fine droplets of hydrochloric acid.

Nitrides. The nitrides of certain metals, such as Mg_3N_2, Li_3N, Ca_3N_2, are decomposed by water to form the corresponding hydroxide and liberate ammonia gas—

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

When magnesium is burnt in air, it forms mainly MgO together with a small amount of the yellow magnesium nitride Mg_3N_2. On subsequent treatment with water the magnesium nitride decomposes and the odour of ammonia is easily recognized.

Hydrides. The hydrides of the alkali and alkaline earth metals are immediately decomposed by water, often explosively, to liberate hydrogen and form the hydroxide of the metal—

$$NaH + H_2O = NaOH + H_2$$

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$

The amides of these metals also react vigorously with water, and like the corresponding nitrides liberate ammonia—

$$\underset{\text{sodamide}}{NaNH_2} + H_2O = NaOH + NH_3$$

It is important, therefore, to note that in the preparation of the hydrides, nitrides and amides of the more reactive metals moisture must be rigidly excluded.

Water of Crystallization

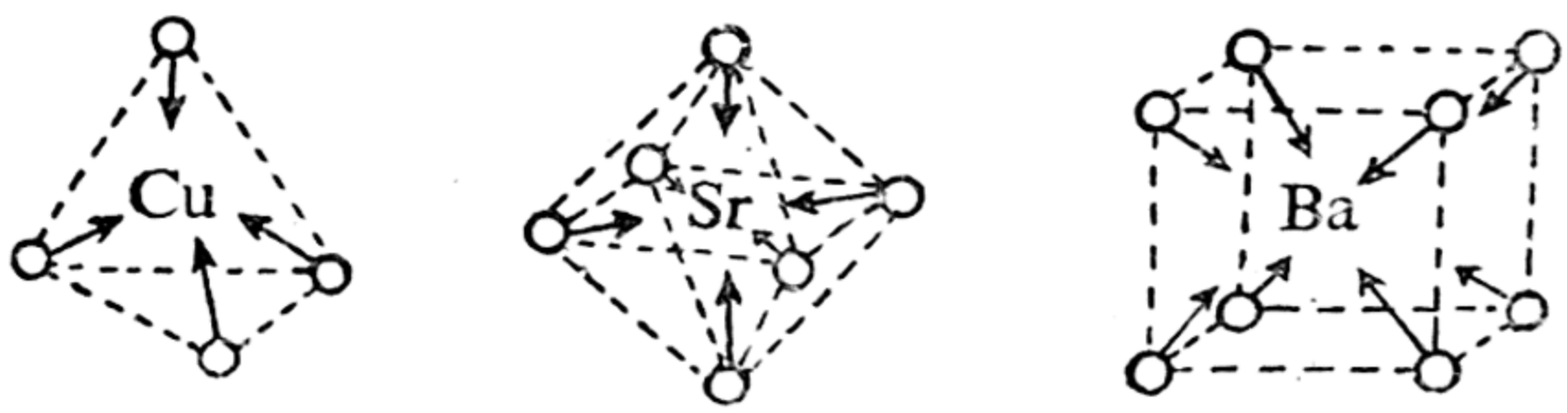
When a solution of copper sulphate in water is concentrated and allowed to crystallize, clear blue crystals are obtained which have the molecular formula $CuSO_4 . 5H_2O$. Each molecule of copper sulphate crystallizes with five molecules of water. This water is referred to as water of crystallization since its presence in the solid structure is necessary for the formation of crystalline copper sulphate. When these blue crystals are heated, the water of crystallization escapes as water vapour, and the crystals crumble into a white amorphous (that is, non-crystalline) powder. It is important to realize that water of crystallization is not present in the liquid form in which we usually regard water, but as individual molecules each of which plays its part in building up (during crystallization) the regular structure which characterizes the crystalline state. Removal of these individual molecules of water causes a breakdown of this structure and leaves the non-crystalline anhydrous (that is, without water of crystallization) substance, $CuSO_4$.

The number of molecules of water of crystallization varies from one salt to another, for example, $Na_2CO_3 . 10H_2O$, $FeSO_4 . 7H_2O$, and $Cr_2(SO_4)_3 . 18H_2O$, but for any particular salt the number is fixed. Some examples of crystalline salt hydrates are given below, together with their common and chemical names—

Washing soda, or sodium carbonate decahydrate, $Na_2CO_3 . 10H_2O$
Epsom salts, or magnesium sulphate heptahydrate, $MgSO_4 . 7H_2O$
Glauber salts, or sodium sulphate decahydrate, $Na_2SO_4 . 10H_2O$
Borax, or sodium borate decahydrate, $Na_2B_4O_7 . 10H_2O$
Alum, or potassium aluminium sulphate hydrate, $KAl(SO_4)_2 . 12H_2O$
Mohr's salt, or ferrous ammonium sulphate hexahydrate, $(NH_4)_2SO_4 . FeSO_4 . 6H_2O$

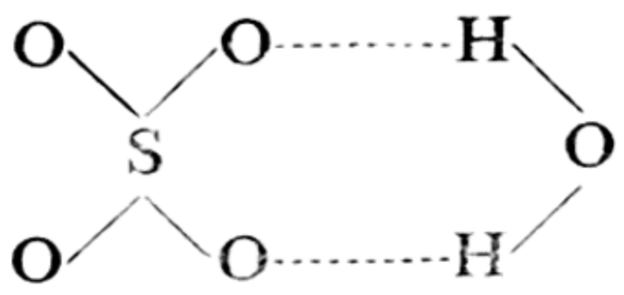
Certain solid acids, for example, oxalic acid, $H_2C_2O_4 . 2H_2O$, and some hydroxides and oxides, for example, $Ba(OH)_2 . 6H_2O$ and $Al_2O_3 . H_2O$, also contain water of crystallization.

The molecules of water in crystalline hydrates fulfill a structural role; they fill voids in the crystal structure and so permit the salt-ions (such as Cu^{++} and SO_4^{--}) to take up a regular (and, therefore, crystalline) arrangement of minimum energy content. The number of molecules of water required for this purpose is very largely determined by the relative sizes of the respective ions. Thus a small ion tends to surround itself with a certain number of molecules of water so as to increase its apparent size as closely as possible to that of the other salt-ion. Regarding each molecule of water as a sphere, it is not difficult to see that the number of molecules required for this purpose will probably be four (tetrahedral arrangement), six (octahedral arrangement) or eight (cubic arrangement), viz.—



Examples occur in strontium chloride with the structure $[Sr(H_2O)_6]Cl_2$, and potash alum with the structure $[K(H_2O)_6]\ [Al(H_2O)_6] . (SO_4)_2$. Where the ions are approximately of the same size the need for this artificial increase in size by hydration does not occur, and crystallization occurs without hydration as, for example, with sodium chloride or common salt, NaCl, which forms beautiful cubic crystals.

There are two extreme schools of thought concerning the mode of linkage of water molecules in crystalline hydrates. On the one hand there is the Co-ordination Theory of Werner as elaborated by Sidgwick, and on the other hand the Electrostatic Theory of Fajans, Born and others. According to the former theory, the molecules of water are considered to be attached by definite valency bonds to their respective salt-ions. The water associated with the cation is considered to be linked through the oxygen portion of the molecule by a co-ordinate-link (dative or semi-polar double bond), i.e. $M^+ \leftarrow OH_2$; that to the anion by some form of "hydrogen" bond, thus—



The second theory does not envisage a definite linkage of the water molecules to the salt-ions in the crystal hydrate, but regards them as being

held in place by the electrostatic forces between the salt-ions. Probably neither theory is completely correct, although on balance the electrostatic theory appears slightly the more probable.

Deliquescence and Efflorescence. Some hydrates on exposure to the atmosphere slowly lose some or all of their water of crystallization and crumble to a powder. Such substances are said to be effloresc ent, the process of losing the water of crystallization being referred to as efflorescence. A familiar example is found in the case of washing soda crystals. On a relatively dry day, the crystals effloresce and become covered with a white opaque powder of sodium carbonate monohydrate

$$Na_2CO_3 . 10H_2O \rightarrow Na_2CO_3 . H_2O + 9H_2O$$

Other examples include copper sulphate pentahydrate, sodium sulphate decahydrate and sodium alum—

$$CuSO_4 . 5H_2O \rightarrow CuSO_4 . H_2O + 4H_2O$$

$$Na_2SO_4 . 10H_2O \rightarrow Na_2SO_4 + 10H_2O$$

The reverse process of taking up moisture from the atmosphere occurs with hygroscopic substances. When this process of taking up moisture results ultimately in the formation of a *solution* of the substance, the term deliquescence is used, and the substance is said to deliquesce. All deliquescent substances are hygroscopic, but not vice versa. Examples of deliquescent substances include sodium hydroxide, calcium chloride and zinc chloride.

The factors which determine the behaviour of a hydrate on exposure to the atmosphere* are—

(*a*) the pressure of aqueous vapour in the atmosphere,
(*b*) the equilibrium aqueous vapour pressure of the hydrate, and
(*c*) the aqueous vapour pressure of a saturated solution of the substance at the same temperature as (*a*) and (*b*).

If, for a given hydrate, (*b*) is appreciably greater than (*a*), then the hydrate will lose water vapour to the atmosphere and will therefore effloresce. If, on the other hand, (*b*) is less than (*a*), the hydrate will tend to absorb water vapour from the atmosphere and will be hygroscopic. If, in addition, (*c*) is less than (*a*) the further process of deliquescence will occur until a solution is produced whose vapour pressure just equals that of (*a*). Since the pressure of the aqueous vapour of the atmosphere is continually varying, being relatively high on wet days and relatively low on dry days, it is not difficult to appreciate that a substance such as $CuSO_4 . 5H_2O$ which has a vapour pressure between these extremes, may

* *See also* p. 199

be completely stable on a wet day but will effloresce on a dry day. Conversely, anhydrous copper sulphate may be stable on a dry day but on a wet day the increased humidity or vapour pressure of the atmosphere will result in hydration and the formation of blue copper sulphate pentahydrate.

Heavy Water. For a discussion of heavy water or deuterium oxide, *see* p. 374.

CHAPTER 19

THE ELEMENTS OF GROUP I

GROUP IA of the Periodic Table comprises the group of elements known as the "Alkali Metals"; these are lithium, sodium, potassium, rubidium and caesium.

ALKALI METALS

In respect of electronic configuration the alkali metals follow the inert gases which possess a very stable structure, the former having a single electron in their outermost shell. This electron the alkali metals may lose readily so forming stable, electropositive, monovalent ions. As may be inferred from the general similarity of the electronic structure of the atoms and of the ions of the alkali metals there is a general similarity between the compounds of this group of elements. It should however be noted that on account of the progressive increase in the size of the atoms of the alkali metals as the atomic weight increases there tend to be progressive modifications in the properties of certain compounds. Some of the chief physical properties of the alkali metals are given in Table 77 on p. 418.

The chief characteristics of the alkali metals may be summarized as follows—

(*a*) All the alkali metals are highly reactive elements standing at the negative end of the electrochemical series (*see* p. 272). They are so reactive that they are capable of decomposing water with considerable violence, hydrogen being evolved. The heat is sufficient in most cases to cause ignition of the evolved hydrogen.

(*b*) The alkali metals are all powerful reducing agents. For example, sodium was formerly employed to obtain aluminium from its chloride by thermal reduction as follows—

$$3Na + AlCl_3 = 3NaCl + Al$$

(*c*) The oxides and hydroxides are all strongly basic, in fact they are the strongest bases known. The oxides and peroxides are formed by the direct union of the alkali metals and oxygen. The hydroxides are formed when the alkali metals react with water, thus—

$$2Na + 2H_2O = 2NaOH + H_2$$

The hydroxides possess an ionic structure like the salts. The violence of the reaction increases with increasing value of the atomic weight of the alkali metal involved. The oxides of the alkali metals cannot (with the

exception of lithium oxide) be obtained by heating the nitrate or the carbonate.

TABLE 77

Some Physical Properties of the Alkali Metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs
Atomic number	3	11	19	37	55
Electronic configuration	2, 1	2, 8, 1	2, 8, 8, 1	2, 8, 18, 8, 1	2, 8, 18, 18, 8, 1
Atomic weight	6·94	22·997	39·096	85·48	132·91
Density (g/cm³ at 20°C)	0·53	0·97	0·86	1·53	1·9
Atomic volume (cm³/g atom)	13·1	23·70	45·50	55·87	69·95
Melting point (°C)	186·0	97·50	62·30	38·30	26·00
Boiling point (°C) (760 mm pressure)	1372·0	886·70	773·90	700·00	510·00
Thermal conductivity (cal./cm²/sec at 20°C)	0·17		0·237		
Electrical resistivity (microhm-cm)	8·50	22·76	7·00	10·00	20·00
Normal electrode potential (volts) (Hydrogen scale)	− 3·02	− 2·712	− 2·922	− 2·928	

(*d*) The normal salts of the alkali metals with strong acids are practically unhydrolyzed and, in general, react neutral.

(*e*) With very few exceptions all the salts are freely soluble in water.

(*f*) The alkali metals combine with hydrogen to form hydrides which are salt-like in nature, e.g. LiH.

(*g*) Except when derived from a coloured acid (e.g. chromic acid, permanganic acid) the salts of the alkali metals are devoid of colour.

(*h*) Each of the alkali metals forms only one stable series of compounds in which the metal in monovalent. Peroxides and polysulphides, etc., are known but these are comparatively unstable compounds.

LITHIUM

Occurrence. Lithium does not occur in the free state in nature, nor are its compounds very abundant. The chief minerals from which commercial supplies of lithium are obtained are—

Spodumene, $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$; 4–8 per cent Li_2O
Amblygonite, $Li(AlF)PO_4$; 9–10 per cent Li_2O

Lepidolite, a lithium mica; a complex silicate of lithium, potassium and aluminium; 2–6 per cent Li_2O

Most of the world's spodumene is obtained from South Dakota in the U.S.A. Important deposits of spodumene and amblygonite are found near Winnipeg in Manitoba. Lepidolite is often found in tin veins in the Eastern United States, South-West Africa and Saxony.

In addition to the above mineral sources large amounts of crude dilithium sodium phosphate, Li_2NaPO_4, are obtained during the recovery of sodium and potassium salts from Searles Lake, California, U.S.A. The crude double lithium sodium salt contains up to 20 per cent Li_2O.

The chief uses of lithium ores are—

(*a*) for the preparation of lithium salts,
(*b*) for the manufacture of special glasses and ceramics, and
(*c*) for the extraction of metallic lithium.

Extraction of Lithium. Metallic lithium is obtained by electrolysis of the fused chloride using a carbon anode and an iron cathode.

Properties of Lithium. Lithium is the lightest metal known; its density is 0·53 g/cm^3. When freshly prepared the metal exhibits a bright silvery surface, but the surface quickly tarnishes when exposed to a damp atmosphere. Lithium is softer than lead, but harder than the other alkali metals. Lithium is the least reactive of the alkali metals, although it readily decomposes water. When heated in the air, lithium first melts (m.p. = 186°C) and then takes fire, burning with a bright white flame and forming lithium oxide. Lithium has a great affinity for most elements which may occur as non-metallic impurities or gases in metals and alloys.

Uses of Lithium. The uses of lithium have increased very considerably during recent years. For example increasing applications are being found for lithium alloys. For instance the use of lithium as a 50-50 Ca-Li alloy for the de-oxidation of high conductivity copper castings is widely employed. This is an example of the use of lithium dependent upon its high reactivity towards non-metallic impurities and gases, such as hydrogen and sulphur.

As an alloying element it is added to metals of higher melting point such as aluminium, magnesium, lead and zinc to improve certain of their physical properties such as hardness and tensile strength.

One of the most interesting applications of lithium, however, is for heat-treatment furnace atmospheres where it is claimed it provides a certain method of preventing scaling and surface decarbonization of steel. The *lithium atmosphere* is obtained by passing a "cracked" mixture of air and propane through a lithium cartridge maintained at a temperature of 650–810°C. This cartridge contains a mixture of lithium chloride and lithium carbonate mixed with a small amount of metallic lithium, the whole being contained in a sheet steel cup approximately 3 in. in diameter

and 4 in. long. When heated the lithium salts volatilize and lithium vapour is picked up by the cracked propane-air mixture as it flows through the cartridge. The mixture then passes into the furnace where it constitutes a neutral atmosphere.

Lithium Compounds

Lithium hydride, LiH, is formed when lithium is heated in an atmosphere of hydrogen. It is of interest to note that electrolysis of the fused hydride liberates hydrogen at the *anode*. When acted upon by water the hydride evolves hydrogen with the accompaniment of considerable heat. This reaction has found application in air-sea rescue work when the hydride is contained within a small metal container, and when mixed with a little water liberates sufficient hydrogen to fill a small balloon capable of holding aloft a small radio aerial.

Lithium oxide, Li_2O, is a white powder obtained either by heating the metal in air, or alternatively by heating the hydroxide in an atmosphere in dry hydrogen. Lithium oxide reacts slowly with water to form lithium hydroxide.

Lithium peroxide is made by the action of hydrogen peroxide on lithium hydroxide. The action of water on the metal gives rise to the formation of lithium hydroxide.

Lithium carbonate is precipitated as a white solid when ammonium carbonate solution is added to a solution of a soluble lithium salt.

$$2LiCl + (NH_4)_2\,CO_3 = Li_2CO_3 \downarrow + 2NH_4Cl$$

Lithium carbonate is soluble in the presence of carbon dioxide owing to the formation of lithium bicarbonate, thus—

$$Li_2CO_3 + CO_2 + H_2O = 2LiHCO_3$$

The aqueous solution of lithium bicarbonate is sold for medicinal use under the name of *lithia water*.

Lithium chloride is very similar in general behaviour to sodium chloride although it is more soluble in water than is sodium chloride, and in addition it is extremely deliquescent—in fact, it is possibly the most deliquescent substance known.

Lithium fluoride is only sparingly soluble in water and in this respect resembles the fluorides of the alkaline earth metals.

Lithium phosphate, like the carbonate, is practically insoluble in water.

Uses of the Lithium Compounds. On account of its hygroscopic, non-volatile and non-toxic properties, lithium chloride finds application for dehumidifying air for air-conditioning and also as an industrial drying agent. The chloride and the fluoride are used as fluxes for welding, especially of aluminium and its alloys; for these alloys, however, some workers prefer the fluoride owing to its non-hygroscopic nature.

Lithium hydroxide is used for the mercerizing of cellulose for rayon manufacture.

Lithium stearate and similar lithium soaps find application as lubricants which are required to retain their viscosity over a wide temperature range.

The naturally occurring lepidolite is used in the glass and ceramic industries. The lithium and fluorine occurring in this mineral facilitate the melting of the glass, because of their fluxing action, and also give the product a lower coefficient of thermal expansion, thereby lessening the possibility of fracture when subjected to sudden changes of temperature. When added to the melt in large amounts lepidolite acts as an opacifier.

SODIUM

Occurrence. Although far too reactive to be found free, sodium occurs in nature in immense quantities in comparatively few compounds, the most important being sodium chloride.

Sodium Chloride or Common Salt. This compound, which has been known since earliest time, occurs in nature in two states, (*a*) in the solid state as "rock salt" and, (*b*) in solution, as brine. Rock salt, which makes up 3 per cent of the earth's crust, exists in extensive deposits at Wielicza in Galicia, in the Stassfurt region of Germany, in California, Kansas, Utah and Salt Lake City in the U.S.A., in the Punjab, and at Northwich, Nantwich and Middlewich in Cheshire, and Droitwich in Worcestershire. These deposits of rock salt have been formed by the evaporation of prehistoric seas.

The salt is usually obtained by running water down boreholes and then pumping out the brine when it is nearly saturated with salt. The salt is then obtained by evaporation of the brine.

Sodium chloride is present to the extent of approximately 2·7 per cent in sea water, from which it is obtained by evaporation. The concentration of total solids in sea water is approximately 3·5 per cent. The concentration of sodium chloride in inland seas and in saline springs is, however, often much higher than that obtaining in sea water. Thus, for example, the water of the Dead Sea contains about 9 per cent sodium chloride, the total solids amounting to approximately 22 per cent. The salinity of the Salt Lake of Utah is even higher than that of the Dead Sea.

The reason for the predominance of sodium chloride over potassium chloride in sea water is that potassium chloride is much more readily absorbed by the soil during the passage of the water from springs to rivers and down to the seas; further, sodium, unlike calcium and many other elements carried down into the seas, is not utilized to any extent by marine creatures in the formation of their shells, etc. Thus, sodium chloride tends to accumulate in sea water.

Felspars. Sodium occurs in large quantities in nature in igneous rocks of which some of the most common are the felspars, and in particular

Soda Felspar, or Albite, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$. As a result of weathering, decomposition occurs as follows—

$$Na_2O \cdot Al_2O_3 \cdot 6SiO_2 + CO_2 + H_2O = Na_2CO_3 + \underbrace{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O}_{\text{Kaolin or China clay}} + 4SiO_2$$

Sodium Carbonate. The soluble sodium carbonate is carried away in solution whilst the residue of kaolin and silica remains behind. The accumulation of sodium carbonate in inland seas which have subsequently evaporated has probably led to the formation of deposits of sodium sesqui-carbonate $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, such as those found in Wyoming in the U.S.A., and in Lake Magadi in East Africa. Other forms of the carbonate occurring naturally are Natron, $Na_2CO_3 \cdot H_2O$, and Trona, $Na_2CO_3 \cdot 2NaHCO_3 \cdot 3H_2O$.

All these minerals constitute valuable sources of alkali.

Borax. Certain inland lakes, notably in California and Nevada in the U.S.A., and in certain parts of China, Tibet and Persia contain, in addition to other sodium salts, sodium borate. The boron has probably been derived from thermal springs. Evaporation of these lakes has led to the production of deposits of borax, $Na_2B_4O_7 \cdot 10H_2O$.

Chile Saltpetre. Sodium nitrate mixed with sodium chloride, sodium sulphate and sodium iodate occurs in extensive deposits in the deserts on the borders of Chile and Peru. This particular mineral is known as Chile Saltpetre or Caliche. The nitrogen is possibly of organic origin, being derived, by continual extraction with rain and stream water, from the bird's deposits or guano.

Cryolite. Sodium also occurs in nature as the double fluoride of sodium and aluminium known as cryolite, $3NaF \cdot AlF_3$. Extensive deposits of this mineral occur in Greenland. Cryolite finds considerable technological importance in the extraction of aluminium by the Hall-Héroult process.

Preparation of Sodium. Two processes are employed at the present time for the preparation of metallic sodium, both of which are electrolytic processes.

(*a*) The Castner process.
(*b*) The Down's process.

The Castner Process. In principle the Castner process is the same as that which Davy employed when he first isolated sodium. It consists in essence of the electrolysis of molten sodium hydroxide.

The electrolytic cell employed for this preparation is shown diagrammatically in Fig. 153. Sodium hydroxide is contained in an iron pot *A*, supported in a brickwork setting. The hydroxide is melted by means of a ring of gas jets *B*; the temperature of the electrolyte is maintained at about 20°C above its melting point (i.e. 310°C). An iron cathode *C*

enters the cell through the bottom of the iron pot, being maintained in position by the solidified cake of sodium hydroxide *D*. Nickel anodes *E* are supported from above around the centrally-placed cathode, the anodes being insulated electrically from the iron pot and also from the iron cylinder *F* by means of asbestos washers. A screen of nickel gauze *G* separates the anode and cathode. On electrolysis sodium and hydrogen are liberated at the cathode, the molten sodium, guided by the nickel gauze screen *G* rises and collects in the iron cylinder *F*. The hydrogen also enters this cylinder and forms an atmosphere above the molten sodium, so protecting it from oxidation. From time to time the molten sodium is ladled off by means of a perforated ladle which retains the liquid metal on account of its high surface tension, but permits the molten sodium hydroxide to run through.

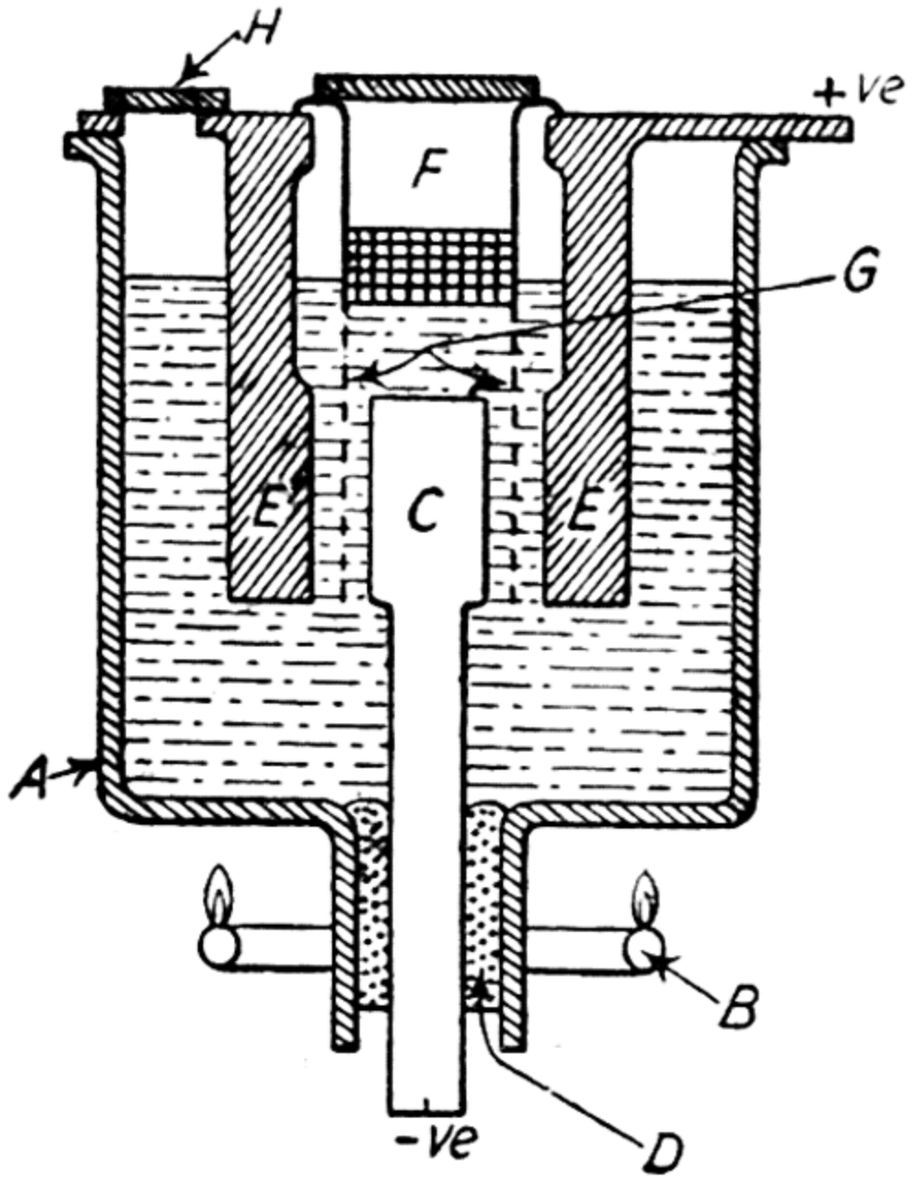


FIG. 153. Castner Cell for the Electrolytic Manufacture of Sodium

Oxygen is liberated at the anode and escapes through the port *H*. The changes occurring during electrolysis may be depicted ionically as follows—

$$NaOH \rightleftharpoons Na^+ + OH' \quad . \quad (a)$$

The hydroxyl ions are discharged at the anode; they then react together thus—

$$4OH = O_2 + 2H_2O \quad . \quad (b)$$

The oxygen escapes as described above. The water dissolves in the molten sodium hydroxide and is then electrolyzed with the production of hydrogen, which is liberated at the cathode with the sodium as shown in equation (*a*), whilst the oxygen is liberated at the anode and passes upwards through the electrolyte and out of the cell through the port *H*.

For a cell holding 100 kilogrammes a typical current would be 1200 amperes at 5 volts. The temperature of the electrolyte must not rise unduly otherwise there would be considerable loss of efficiency due to the sodium dissolving in the molten sodium hydroxide to form a "metallic fog."

The Down's Process. The electrolysis of fused sodium chloride to give its component elements is not practicable owing to the ease with which molten sodium dissolves in the molten electrolyte to give a "metallic fog" as described above in the case of the Castner process. Although the melting point of sodium chloride is 804°C, this may be lowered by the addition of certain salts, such as the chlorides and fluorides of the alkaline earth metals. By means of such additions it is possible to maintain a

bath of molten sodium chloride at temperatures of 600°–650°C. Electrolysis of this electrolyte does not give rise to serious losses of sodium by the formation of metallic fog.

The cell employed in the Down's process is shown diagrammatically in Fig. 154. The shell of the cell *B* is made of steel but is lined with refractory brickwork. The anode *A* is made of graphite and the cathode *C* is in the form of an iron ring. The fused electrolyte *D* nearly fills the cell, further additions of electrolyte being charged through port *E*. On electrolysis, chlorine is liberated at the anode and this gas rises upwards through the electrolyte, through the collecting dome *F* and out of the cell through the pipe *G*. The sodium, which is liberated at the ring cathode, rises upwards through the electrolyte, is collected by the annular sodium collector *H* and thence through pipe *I* to the collecting vessel *J*. The chemical reaction involved in this process is as follows—

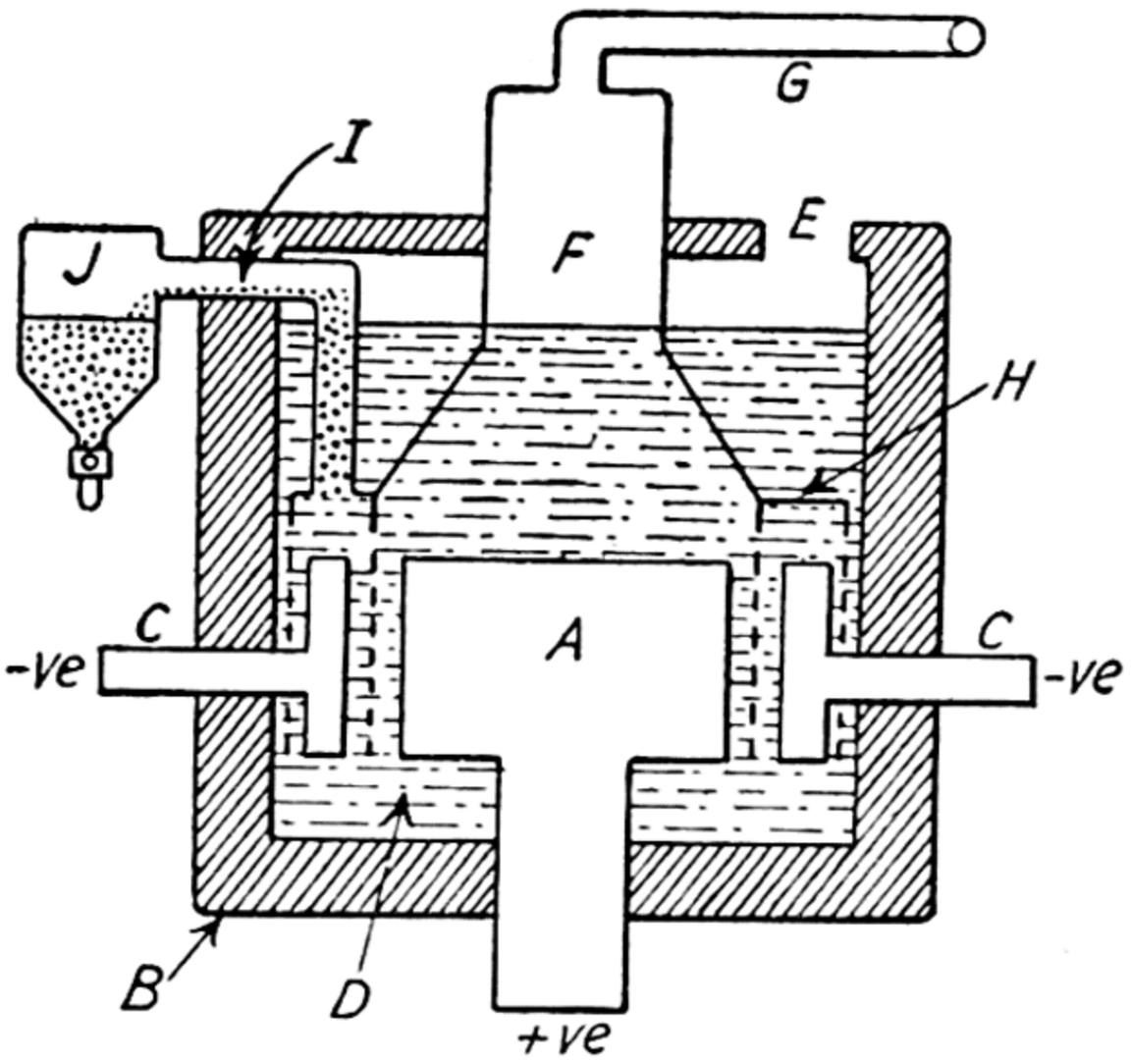


FIG. 154. Down's Cell for the Electrolytic Manufacture of Sodium

$$2NaCl = 2Na + Cl_2$$

Physical Properties of Sodium—

(*a*) Sodium is a silvery-white metal unaffected by dry air at ordinary temperature, but rapidly tarnishing in moist air.

(*b*) It is a soft metal and may be cut readily with a knife. It is easily capable of being pressed and moulded into the form of ribbon and wire.

(*c*) Sodium exhibits a low melting point (97·5°C).

(*d*) It is a good conductor of heat and electricity.

(*e*) Sodium has a low density (0·97) and therefore floats on water.

Chemical Properties of Sodium

(*a*) Sodium is a very reactive metal. Owing to the ease with which it reacts with the moisture of the atmosphere it is necessary either to store it under the surface of a liquid such as naphtha which contains no oxygen, or alternatively to store it in airtight drums.

(*b*) When heated in air, sodium burns readily with a bright yellow flame to form a mixture of oxides, the peroxide predominating.

$$4Na + O_2 = 2Na_2O$$

Sodium monoxide

$$2Na + O_2 = Na_2O_2$$

Sodium peroxide

(*c*) When heated, sodium combines directly with the halogens, phosphorus and sulphur to form the halides, phosphide and the various polysulphides respectively.

When heated in hydrogen, sodium forms its hydride, NaH.

(*d*) Sodium is a strong reducing agent reducing, for example, chlorides of the more refractory elements to the metal, thus--

$$BeCl_2 + 2Na = 2NaCl + Be$$

Sodium reacts similarly with the oxides of metals less reactive than itself.

Thus, sodium reacts with boric oxide as follows—

$$B_2O_3 + 6Na = 3Na_2O + 2B$$

(*e*) When placed on water sodium floats and reacts as follows—

$$2Na + 2H_2O = 2NaOH + H_2$$

The heat of the reaction is sufficient to melt the sodium but unless the water is heated or the metal is in the form of large pieces there is insufficient heat to ignite the hydrogen.

(*f*) Sodium reacts readily with ethyl alcohol to form sodium ethoxide (or sodium ethylate) and liberate hydrogen, thus—

$$2Na + 2C_2H_5OH = 2C_2H_5ONa + H_2$$

This reaction is sometimes used for the preparation of a standard solution of sodium hydroxide since on dilution with water the sodium ethoxide reacts as follows—

$$C_2H_5ONa + H_2O = NaOH + C_2H_5OH$$

(*g*) When heated at 300°–400°C in gaseous ammonia, sodium forms sodamide

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$

When water is added to sodamide there is a violent reaction leading to the formation of sodium hydroxide and the liberation of ammonia, thus—

$$NaNH_2 + H_2O = NH_3 + NaOH$$

Sodium dissolves in liquid ammonia to give a blue colloidal solution.

(*h*) Sodium dissolves in mercury to form sodium amalgam.

(*i*) Sodium reacts violently with acids.

Uses of Sodium. Sodium is used in large quantities for the manufacture of sodium peroxide, sodium cyanide and sodamide. Sodium is frequently employed as a powerful reducing agent in organic chemistry; where a less vigorous reducing agent is required, sodium amalgam is used.

About half of the sodium extracted commercially is employed for the production of lead tetraethyl.

Sodium also finds application as a filling for aero-engine exhaust valves, on account of its good thermal conductivity; and also for refining the grain size of aluminium-silicon alloys (e.g. Alpax).

Minor uses include the use of the metal in electric discharge lamps, for certain types of photo-cells, and as a filling for high-temperature thermometers.

Compounds of Sodium

Sodium Hydride, NaH, may be prepared by heating sodium at about 350°C in an atmosphere of dry hydrogen. As in the case of lithium hydride, sodium hydride reacts with water forming sodium hydroxide and liberating hydrogen; and also when fused and electrolyzed it gives hydrogen at the *anode*.

$$NaH \rightleftharpoons Na^+ + H'$$

Sodium hydride combines with carbon dioxide to form sodium formate, as follows—

$$NaH + CO_2 = H\,.\,COONa$$

Oxides of Sodium. Sodium forms two oxides, viz.—

Sodium monoxide, Na_2O; and
Sodium peroxide, Na_2O_2

Sodium Monoxide is formed together with the peroxide when sodium is heated in air or in oxygen. Since it is difficult to obtain pure sodium monoxide in this way, it is more satisfactory to heat sodium azide with either sodium nitrate or nitrite. The reaction involved is as follows—

$$3NaN_3 + NaNO_2 = 2Na_2O + 5N_2$$

Sodium monoxide is a white solid which reacts with water to form sodium hydroxide, as follows—

$$Na_2O + H_2O = 2NaOH$$

It is thus a normal basic oxide.

Sodium Peroxide is manufactured on a commercial scale by passing an excess of air, free from moisture and carbon dioxide, over sodium contained in aluminium trays placed in iron tubes and maintained at a temperature of approximately 300°C. The trays are slowly moved in the opposite direction to the air current. In this way the reaction is kept under control, otherwise there would be the risk of melting the aluminium trays. The reaction involved is—

$$2Na + O_2 = Na_2O_2$$

When freshly prepared, commercial sodium peroxide exhibits a slight yellow colour, but on exposure to the atmosphere it becomes white,

owing to the formation of a superficial layer of sodium hydroxide and carbonate. Pure sodium peroxide however is white in colour.

An important use for sodium hydride is in connexion with the descaling of metals. This "sodium hydride process" may be applied to all metals except those with low melting points, and the metals zinc, aluminium and tin, and their alloys, which are attacked by caustic soda. Sodium hydride is not supplied as such to the descaling plant, but is generated in the plant by a reaction between hydrogen, in the form of cracked ammonia, and metallic sodium. About 2 per cent sodium hydride is present in the bath of fused caustic soda. In use the work is immersed in the caustic soda-sodium hydride bath maintained at a temperature of 350–370°C. After allowing the work to attain the temperature of the bath it is then taken out, allowed to drain, and quenched in water. In this way the scale is readily removed.

Sodium peroxide is not decomposed by heating, being unlike most other peroxides in this respect.

At atmospheric temperatures sodium peroxide reacts with water to form sodium hydroxide and liberate oxygen as follows—

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2$$

If sodium peroxide is added to a mixture of water and ice, the following reaction occurs—

$$Na_2O_2 + 2H_2O \rightleftharpoons 2NaOH + H_2O_2$$

This reaction is reversible since if hydrogen peroxide is added to an ice-cold, concentrated solution of sodium hydroxide, crystals of a hydrated sodium peroxide, $Na_2O_2 . 8H_2O$, separate out.

Sodium peroxide is a powerful oxidizing agent. For example, it combines with carbon monoxide thus—

$$Na_2O_2 + CO = Na_2CO_3$$

It also reacts with carbon dioxide in the following manner—

$$Na_2O_2 + CO_2 = 2Na_2CO_3 + O_2$$

Sodium peroxide may, therefore, be employed for the purification of the air within an enclosed space such as a submarine or a diving bell.

Sodium peroxide will also oxidize sulphides when heated with them, as is shown by the following example—

$$2FeS_2 + 15Na_2O_2 = 4Na_2SO_4 + Fe_2O_3 + 11Na_2O$$

Reactions such as this are often involved in the determination of sulphur in a naturally occurring sulphide. Sodium peroxide oxidizes ammonia to nitrogen and oxides of nitrogen to nitrates.

With acids, sodium peroxide reacts to form the corresponding sodium salt.

Uses of Sodium Peroxide. Sodium peroxide is employed not only for

analytical purposes such as those described above, but also for the bleaching of textiles, for the production of sodium perborate, calcium peroxide, and for the synthesis of dyes and other organic compounds.

It is also employed as a source of oxygen and absorbent of carbon dioxide in confined spaces; in this connexion it is often employed under the commercial name of "Oxone."

Sodium Hydroxide (Caustic Soda), NaOH. Sodium hydroxide is one of the most important of all industrial chemicals. On a commercial scale it is prepared by one of two methods; these are—

(*a*) the electrolysis of brine solution, and
(*b*) the action of milk of lime on sodium carbonate solution.

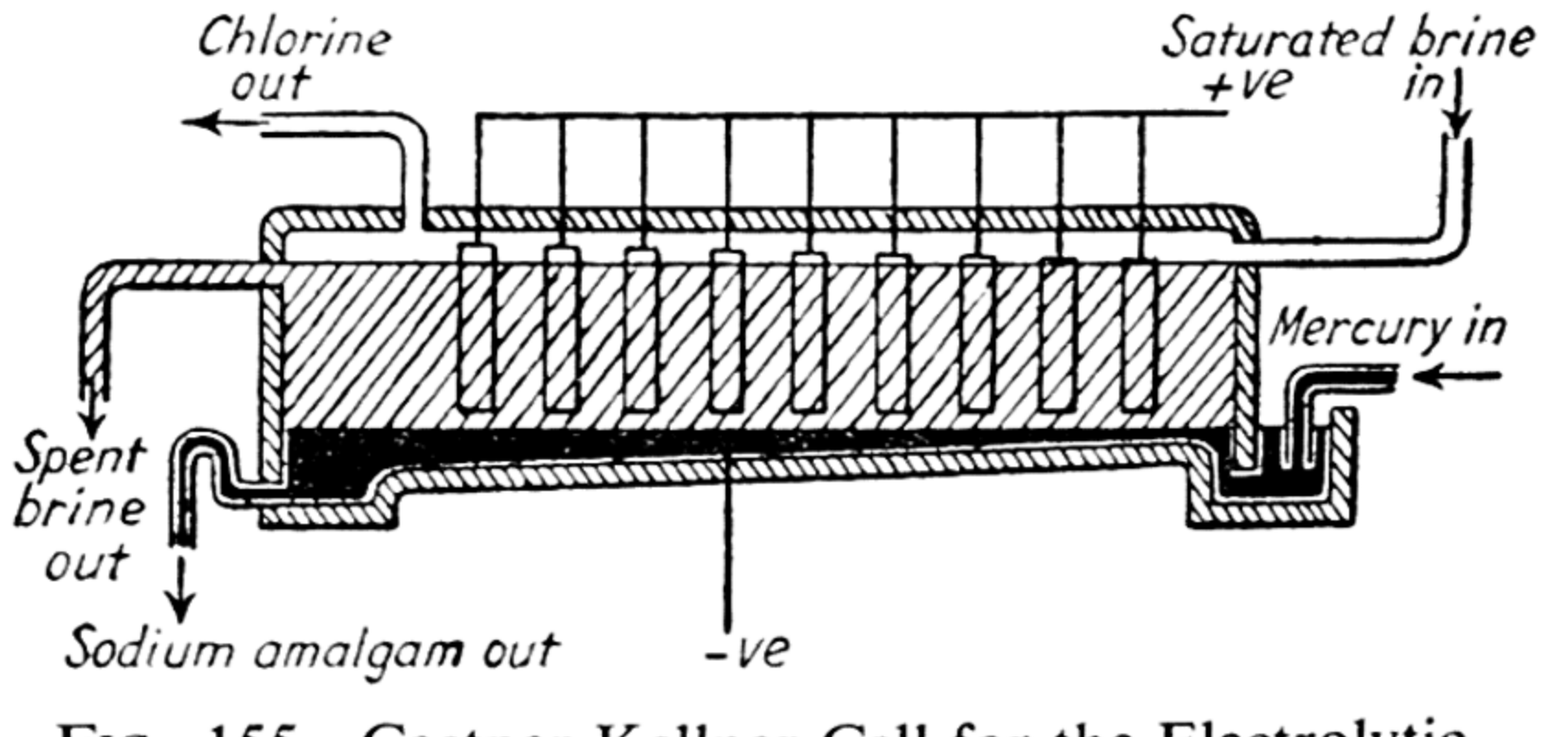


FIG. 155. Castner-Kellner Cell for the Electrolytic Production of Sodium Hydroxide

Electrolysis of Brine Solutions

Electrolytic cells for the production of sodium hydroxide are of two types—

(1) Mercury cathode cells.
(2) Diaphragm cells.

The Castner-Kellner cell is an example of a mercury cathode cell; its construction is shown in Fig. 155. A saturated solution of brine is run into a large rectangular tank made of slate, 4 ft long, 4 ft wide, and 6 in. deep, along the slightly sloping floor of which flows a thin film of mercury. This mercury film serves as the cathode of the cell, whilst a number of graphite plates constitute the anode. Resulting from electrolysis, chlorine is evolved at the anode and is led out of the cell through a duct. The chlorine is then either used at once or dried and collected. At the cathode the sodium ions are discharged where they react with the mercury to form sodium amalgam. The amalgam flows down the floor of the cell and syphons out into a receiving tank containing water where the amalgam reacts to form sodium hydroxide solution and liberate hydrogen. The hydrogen is collected and often caused to react with chlorine to form hydrogen chloride. The spent brine leaving the cell is re-saturated with salt and returned to the cell.

The operation of a diaphragm cell is well illustrated by the Nelson type. This cell consists essentially of a vessel made of compressed asbestos *B* (Fig. 156). This vessel is covered with a steel gauze net *C* which serves as the cathode. The vessel *B* contains the brine to be electrolyzed, and also the carbon anode *A*. The brine in the cell is maintained at a constant level. The whole vessel is contained within an outer casing *D*, through which steam is blown. In use, brine slowly soaks through the asbestos diaphragm inside which it undergoes electrolysis; chlorine ions migrate to the anode, whilst the sodium ions migrate towards the steel gauze cathode. On being discharged at the cathode the sodium reacts with the steam passing through the outer casing *D* to form sodium hydroxide solution and liberate hydrogen which is led off as indicated in Fig. 156. The sodium hydroxide solution is collected at the bottom of the outer casing from whence it is run off for concentration by evaporation.

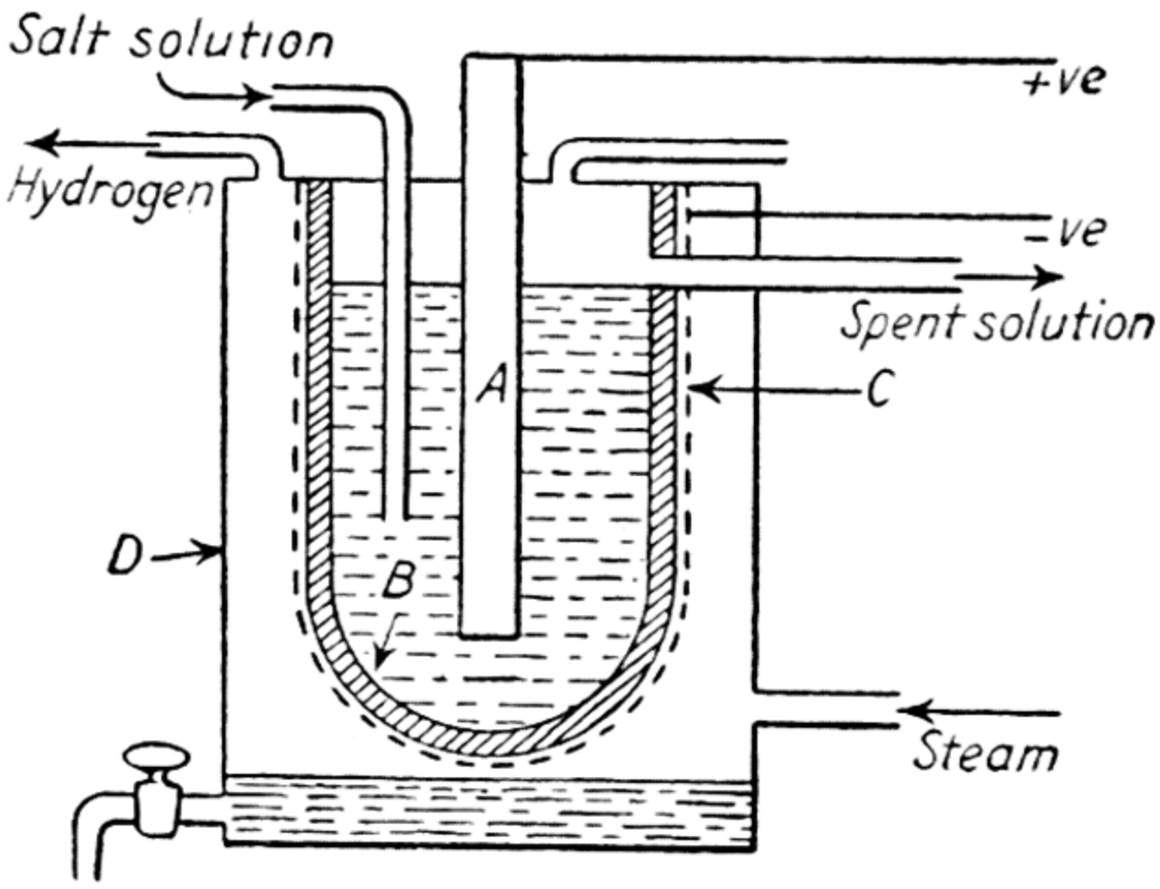


FIG. 156. Nelson Cell for the Electrolytic Manufacture of Sodium Hydroxide

Mercury cathode cells have the advantage over diaphragm cells in that (*a*) they have a higher current efficiency, 10–15 per cent higher, (*b*) a higher concentration of caustic liquor is possible, (*c*) the caustic liquor is pure and free from chloride, (*d*) the cells are smaller, and (*e*) hypochlorite formation, attack of carbon anodes and the presence of impurities like carbon dioxide in the chlorine are reduced to a minimum. On the other hand cells which make use of a mercury cathode suffer from the high capital cost of the mercury.

The Action of Milk of Lime on Sodium Carbonate Solution

Gossage's Method. In this method a 10 per cent solution of sodium carbonate is boiled with lime, when the following reaction occurs—

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 \downarrow + 2NaOH$$

Calcium carbonate is precipitated as indicated above.

For successful production Gossage's method requires a source of cheap sodium carbonate. Originally this process, introduced about a century ago, was the only process for the production of caustic soda, but at a later date electrolytic methods came to the forefront since they employ brine as raw material. However, with the advent of cheap sodium carbonate from

the Solvay process (*see* p. 432), Gossage's method has again assumed a dominant position.

It should be noted that the reaction is reversible in nature, and working conditions have to be adjusted very carefully in order to obtain the highest efficiency. The temperature of the solution is raised to boiling point by blowing in steam, the caustication being conducted in large iron tanks having mechanical stirrers. After the reaction is complete, the calcium carbonate is allowed to settle and the clear liquor run off and concentrated and, if desired, evaporated to dryness. The caustic soda is fused and either run into stick moulds, or kegs, or alternatively pelletted.

Physical Properties of Sodium Hydroxide

(*a*) Sodium hydroxide is a white crystalline solid.

(*b*) It melts easily (318°C) and may be cast into the form of sticks or pellets in which form it is often marketed.

(*c*) Sodium hydroxide is readily soluble in water and its solution is accompanied by the evolution of considerable heat. It is only sparingly soluble in ethyl alcohol, however, and differs in this respect from potassium hydroxide.

(*d*) Sodium hydroxide is very deliquescent, absorbing considerable moisture when exposed to the air. It also absorbs carbon dioxide to form sodium carbonate.

Chemical Properties of Sodium Hydroxide

(*a*) Sodium hydroxide is a very strong alkali.

(*b*) It precipitates many metallic hydroxides from solutions of metallic salts, thus—

$$CuSO_4 + 2NaOH = Cu(OH)_2\downarrow + Na_2SO_4$$
$$FeCl_3 + 3NaOH = Fe(OH)_3\downarrow + 3NaCl$$

In certain cases, however, the metallic hydroxide dissolves in excess of sodium hydroxide solution, as in the following two examples—

(i)
$$ZnSO_4 + 2NaOH = Zn(OH)_2\downarrow + Na_2SO_4$$
$$Zn(OH)_2 + 2NaOH = \underset{\text{sodium zincate}}{Na_2ZnO_2} + 2H_2O$$

(ii)
$$AlCl_3 + 3NaOH = Al(OH)_3\downarrow + 3NaCl$$
$$Al(OH)_3 + NaOH = \underset{\text{sodium aluminate}}{NaAlO_2} + 2H_2O$$

(*c*) Hot aqueous solutions of sodium hydroxide react with aluminium and with zinc forming their respective aluminates or zincates and liberating hydrogen.

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2\uparrow$$
$$Zn + 2NaOH = Na_2ZnO_2 + H_2\uparrow$$

Fused sodium hydroxide will also attack most other metals.

(*d*) Sodium hydroxide saponifies fats to give alcohols and soaps (i.e. sodium salts of fatty acids). In equation form this may be written—

A fat + caustic soda = an alcohol + a soap

or in more specific form, considering mutton fat which contains glyceryl stearate—

$$\begin{array}{l} CH_2OOC \cdot C_{17}H_{35} \\ | \\ CHOOC \cdot C_{17}H_{35} \\ | \\ CH_2OOC \cdot C_{17}H_{35} \end{array} + 3NaOH = \begin{array}{l} CH_2 \cdot OH \\ | \\ CH \cdot OH \\ | \\ CH_2 \cdot OH \end{array} + 3C_{17}H_{35} \cdot COONa$$

Glyceryl stearate (tristearin) — glycerine — sodium stearate (a soap)

(*e*) Either in aqueous solution or in the solid condition sodium hydroxide slowly attacks glass and porcelain.

(*f*) With elements occurring in Groups V to VII of the Periodic Classification, sodium hydroxide reacts to give either the hydride or the sodium derivative of the element, but no hydrogen is evolved. The following examples illustrate this—

$$4P + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2$$

$$4S + 6NaOH = 2Na_2S + Na_2S_2O_3 + 3H_2O$$

$$Cl_2 + 2NaOH = NaCl + NaClO + H_2O \text{ (in cold solution)}$$

$$3Cl_2 + 6NaOH = 5NaCl + NaClO_3 + 3H_2O \text{ (in hot solution)}$$

(*g*) Caustic soda readily destroys living tissue. It is for this reason that it is termed "caustic" soda. Great care therefore should be taken when handling this compound.

Uses of Sodium Hydroxide. Sodium hydroxide is used in very large quantities for the manufacture of soap. It also finds considerable application for the mercerizing of cotton and in the paper-making and dyeing industries. Further uses for caustic soda are in the bleaching trades and in the Bayer process for the purification of bauxite prior to electrolysis in the Hall-Héroult furnace (*see* p. 543).

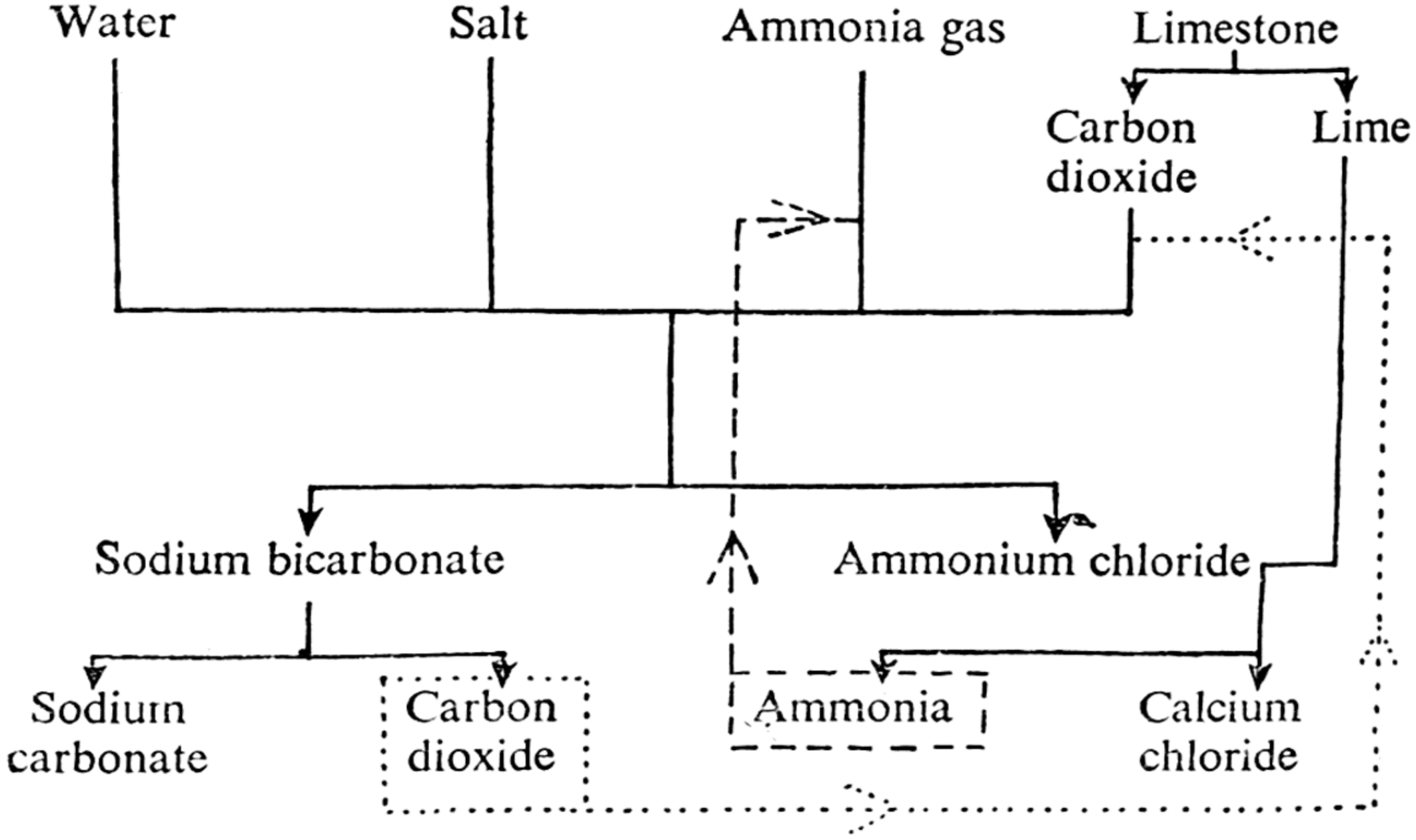
Caustic soda is also the raw material used for the manufacture of many sodium compounds. Other uses include its application for the refining of petroleum and in the tanning, rayon and rubber industries.

Sodium Carbonate, Na_2CO_3. Sodium carbonate used to be manufactured by the Le Blanc process in which salt was heated with sulphuric acid to form "salt cake." This in turn was heated with coal and limestone to form a "black ash" from which the sodium carbonate was leached out. The Le Blanc process, however, has now been rendered obsolete by the introduction of the Solvay or Ammonia-Soda process. It is the intention, therefore, only to describe this latter process here.

The Solvay or Ammonia-Soda Process

The principle of this process is that sodium bicarbonate is precipitated from a mixed solution of brine and ammonium carbonate saturated with carbon dioxide, and on subsequently heating the sodium bicarbonate the normal salt is obtained.

The flow sheet for this process is given below—



It is important to note that the success of the Solvay process depends upon the comparatively low solubility of sodium bicarbonate in water, particularly in the presence of excess carbon dioxide.

When a concentrated solution of sodium chloride is saturated first with ammonia, and then with carbon dioxide, the ammonium carbonate first formed reacts with the sodium chloride to produce sodium carbonate. This, in turn, in the presence of excess carbon dioxide, reacts to form sodium bicarbonate which is precipitated. The reactions involved may be depicted thus—

$$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + 2NaCl = Na_2CO_3 + 2NH_4Cl$$
$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3 \downarrow$$

The actual manufacturing process is as follows. Brine is allowed to pass downwards through a scrubber (*see* Fig. 157) which consists of a number of compartments so constructed that the brine forms a layer in each compartment, running down pipes from one floor to the next lower floor, whilst ammonia passes upwards, under the domes or "mushroom" baffles, through the brine and so on to the next higher floor. In this way

the concentrated ammonia meets the nearly-saturated brine whilst the exhausted ammonia encounters the unsaturated brine. Since this process of saturation with ammonia is exothermic it is necessary to cool the ammoniacal brine by passing over pipes which are cooled by causing cold water to circulate through them. The ammoniacal brine is then allowed to run down a carbonating tower up which a stream of carbon dioxide is allowed to pass.

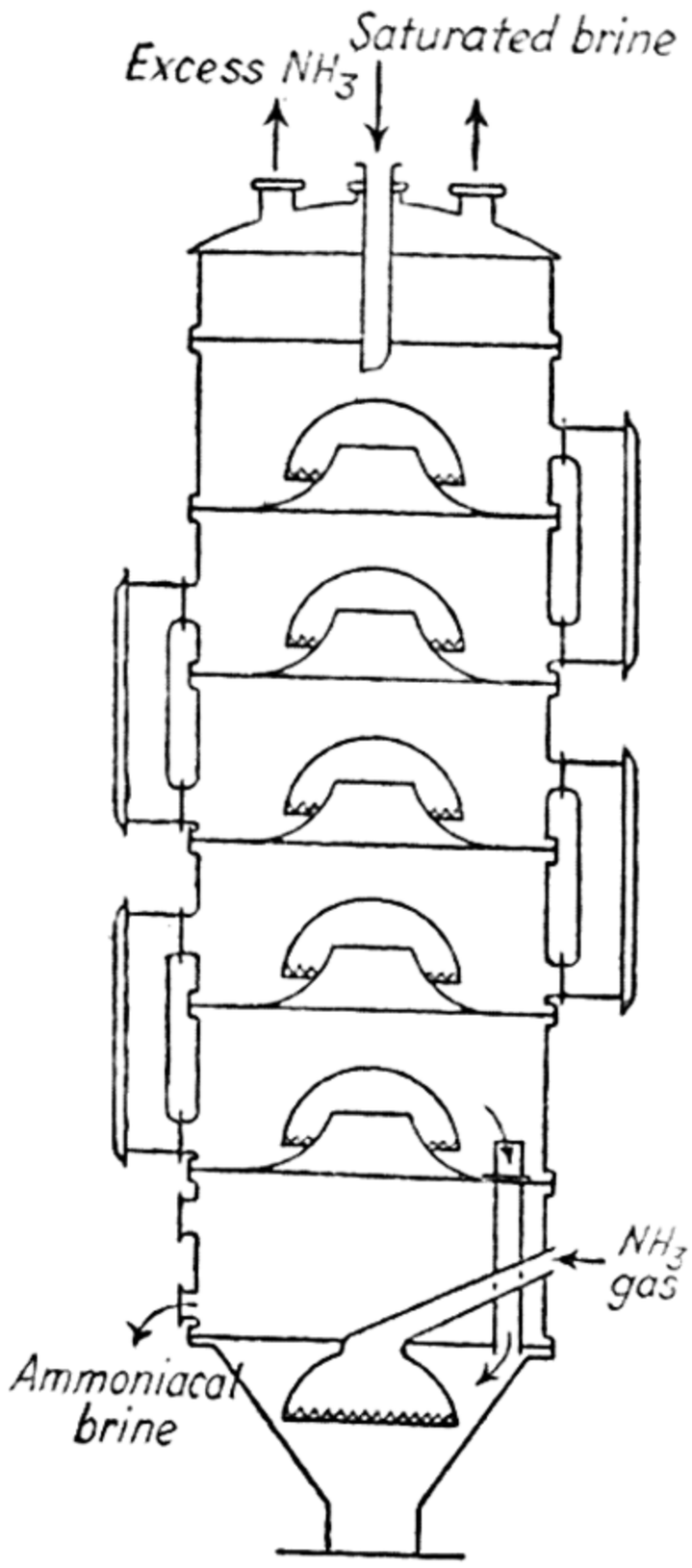


FIG. 157. Ammonia Absorption Tower

The construction of the carbonating tower is shown in Fig. 158. The carbonating tower is from 70–90 ft high and 5–7 ft diameter. It is in this carbonating tower that sodium bicarbonate and ammonium chloride are formed, the former being removed from the bottom of the tower in the form of a fine suspension. The reactions occurring in the carbonating tower are exothermic, and since the solubility of sodium bicarbonate increases with rising temperature it is necessary to cool the carbonating tower. In the initial stages the temperature is not allowed to rise above 30°–40°C, but in the final stages the temperature is maintained at approximately 15°C in order to effect maximum separation of sodium bicarbonate as a sludge. The sodium bicarbonate is separated from the solution by filtration, rotary filters often being employed for this purpose, and then on heating of the residue the normal salt, sodium carbonate, is obtained, as indicated by the following equation—

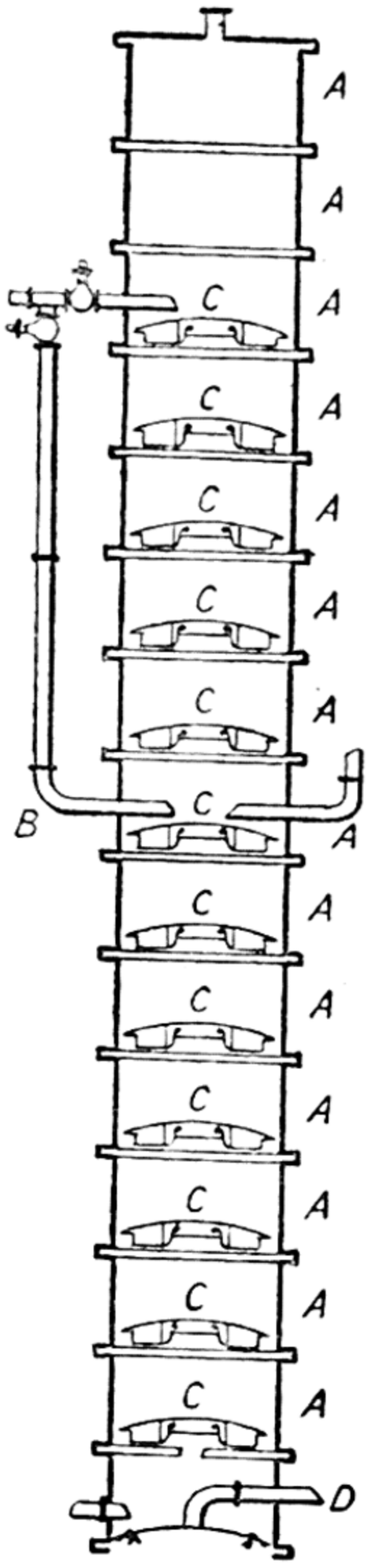


FIG. 158. Carbonating Tower

$$2NaHCO_3 = Na_2CO_3 + H_2O \uparrow + CO_2 \uparrow$$

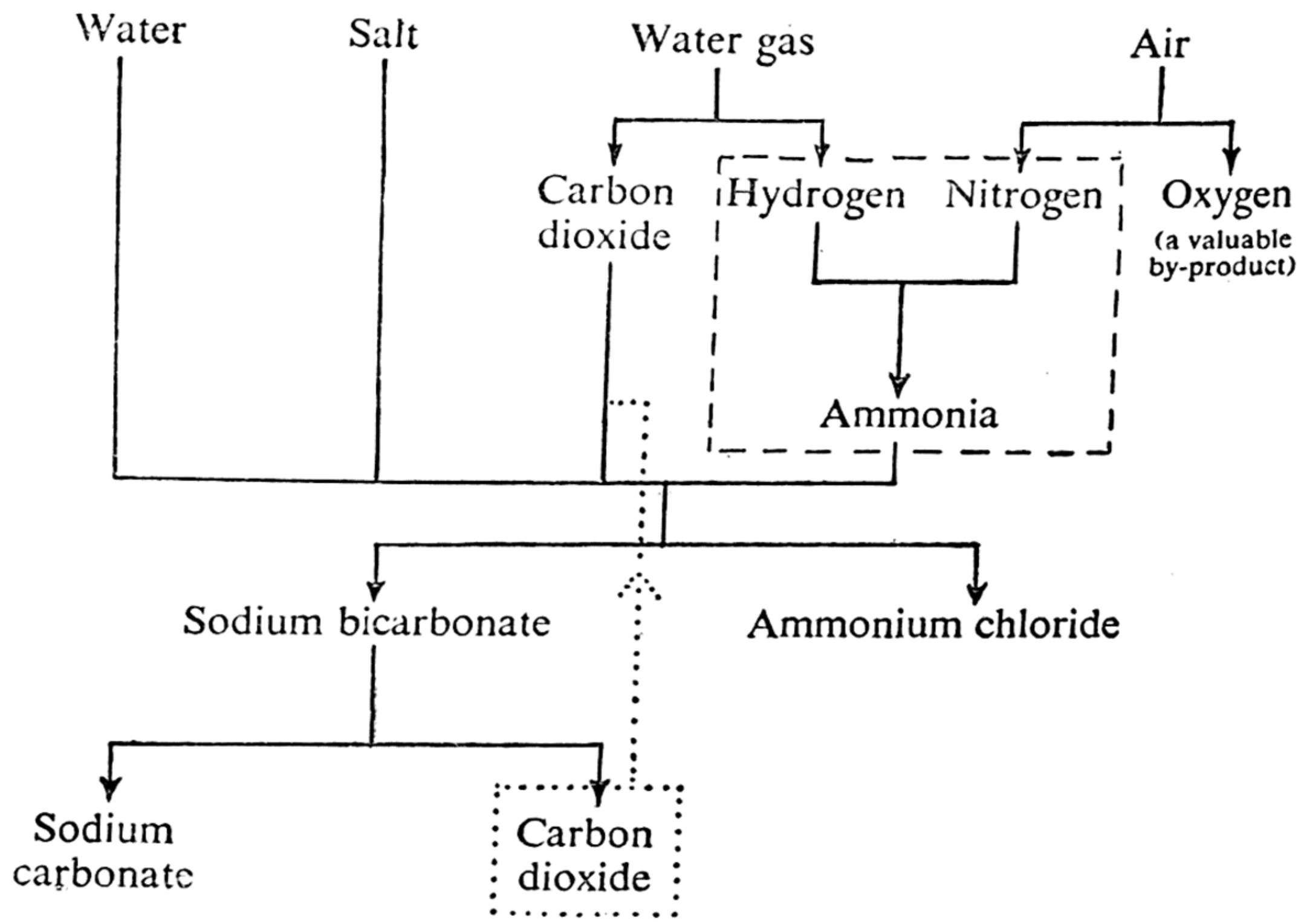
The product of this calcination is often known as *soda ash*.

One of the advantages of the Solvay process is that it is to a large extent self-contained. Thus, the limestone which is calcined to provide the carbon dioxide necessary for the carbonation of the ammoniated brine,

also yields lime. This in turn, on reaction with the ammonium chloride solution (the filtrate after removal of the sodium bicarbonate), yields ammonia gas on heating. Thus, the ammonia necessary for saturation of the brine in the first instance is, except for working losses, kept within the plant. Also, the carbon dioxide evolved during the calcination of the sodium bicarbonate to sodium carbonate is returned to the plant for use in the carbonating tower.

The calcium chloride left after the regeneration of the ammonia by interaction with the lime is a waste product and although there are some commercial applications for this substance it tends to accumulate on the market. Typical uses include its application for the manufacture of "filling" for paper manufacture, and for inclusion in dust-laying materials on account of its deliquescent properties.

Attempts have been made to merge the Solvay process with the Haber process; in this way no waste products are produced. A much simplified flow sheet of the Solvay-Haber process is given below, the reactants of the Haber process being shown within the broken line.



Other Sources of Sodium Carbonate. Sodium carbonate is also manufactured electrolytically, particularly in the U.S.A. Sodium chloride is electrolyzed in a cell of the diaphragm type (*see* p. 429) so forming caustic soda solution and liberating hydrogen and chlorine. Carbon dioxide is

bubbled through the solution thus forming sodium carbonate, which is obtained by crystallization.

It should also be recalled that the naturally occurring deposits of sodium carbonate occurring in East Africa and in Wyoming (U.S.A.) constitute valuable sources of supply.

Physical Properties of Sodium Carbonate

(*a*) Anhydrous sodium carbonate is a white powder.

(*b*) The salt dissolves readily in water and forms a series of hydrates containing one, seven or ten molecules of water of crystallization respectively. Details of these hydrates are given below in Table 78.

TABLE 78

Hydrates of Sodium Carbonate

Formula of Hydrate	Name of Hydrate	Commercial Name	Range of Stability
Na_2CO_3 . . .	—	Soda ash	—
$Na_2CO_3.H_2O$ . .	Monohydrate	Crystal carbonate	Above 35·4°C
$Na_2CO_3.7H_2O$ . .	Heptahydrate	—	32·0°–35·4°C
$Na_2CO_3.10H_2O$ . .	Decahydrate	Washing soda	2·1°–32·0°C

Crystal carbonate is obtained by evaporation from the hot solution, whilst evaporation of the solution below approximately 32°C produces the decahydrate. Anhydrous sodium carbonate may be prepared by heating any of the hydrates or sodium bicarbonate. The anhydrous salt is deliquescent, taking up water to form the monohydrate.

Chemical Properties of Sodium Carbonate

(*a*) When heated, sodium carbonate melts but does not suffer decomposition.

(*b*) In aqueous solution the salt undergoes hydrolysis (*see* p. 318), thus—

$$Na_2CO_3 \rightleftharpoons Na^+ + CO_3''$$
$$H_2O \rightleftharpoons H^+ + OH'$$
$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3''$$

Thus, the progressive removal of the H^+ ions by the CO_3'' ions to form the feebly dissociated carbonic acid leaves a preponderance of OH' ions in the solution, which thus reacts alkaline to indicators.

(*c*) On exposure to air, aqueous solutions of sodium carbonate absorb carbon dioxide with the formation of sodium bicarbonate, thus—

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$$

(*d*) If a mixture of sodium carbonate and a salt of a metal less electropositive than sodium are heated, a reaction occurs of which the following is typical—

$$Na_2CO_3 + CuSO_4 \rightleftharpoons Na_2SO_4 + CuCO_3$$

The carbonate thus produced is then decomposed in the following manner—

$$CuCO_3 = CuO + CO_2 \uparrow$$

It is to be noted that the equilibrium between the carbonates and sulphates is moved to the right, with the result that the metallic salt is quantitatively converted into the oxide. This reaction is frequently employed in chemical analysis with the object of "opening up" for analysis metallic salts which are insoluble in water.

Sometimes a mixture of sodium carbonate and potassium carbonate in equimolecular proportions is employed for this purpose; the mixture of these two carbonates has the advantage over sodium carbonate when used alone in that the mixture melts at a lower temperature, i.e. 690°C, against the higher melting point of 851°C for sodium carbonate.

Uses of Sodium Carbonate. Sodium carbonate, in the form of soda ash, is used in large quantities for the softening of hard water (*see* p. 511). It is also employed in the manufacture of glass, water glass, borax, and caustic soda by Gossage's method. Sodium carbonate is also the raw material used for the manufacture of many other sodium compounds. In addition sodium carbonate is a constituent of many proprietary soap powders used for washing clothes.

An important use for sodium carbonate in the form of soda ash is in connexion with the refining of iron and steel, particularly with reference to desulphurization and dephosphorization. For desulphurization the molten metal is tapped into a ladle and granular soda ash thrown in; the proportion of soda ash varies from 0·5 to 2·0 per cent of the weight of metal undergoing treatment. Sufficient time is allowed for the desulphurizing reactions to occur and then as much of the soda slag as possible removed by skimming and careful tilting of the ladle. The reactions occurring are as follows—

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \uparrow \quad . \quad . \quad . \quad (a)$$

Reaction (*a*) occurs by virtue of dissociation at the high temperatures which obtain.

The actual removal of the sulphur is then effected according to reactions (*b*) and (*c*)—

$$Na_2O + \begin{matrix}MnS\\FeS\end{matrix} = \begin{matrix}MnO\\FeO\end{matrix} + Na_2S \quad . \quad . \quad . \quad (b)$$

$$Na_2CO_3 + Na_2S + \begin{matrix}MnO\\FeO\end{matrix} = \begin{matrix}Mn\\Fe\end{matrix} + SO_2 + CO + 2Na_2O \quad . \quad (c)$$

Some measure of dephosphorization is also obtained by treatment with soda ash in the amounts normally employed for desulphurization, but increased dephosphorization can be obtained by the use of a mixture of iron oxide (mill scale) and soda ash.

Sodium Bicarbonate, $NaHCO_3$. Sodium bicarbonate is manufactured from the crude salt obtained as a sludge in the carbonating towers of the Solvay process. This crude material is purified, by washing with water to remove sodium chloride and ammonium salts, and then dissolved in water. This solution is then heated by steam coils in order to expel ammonia and carbon dioxide. After filtration the solution is treated with carbon dioxide and the precipitated sodium bicarbonate filtered off and dried.

Physical Properties of Sodium Bicarbonate

(*a*) Sodium bicarbonate occurs in the form of small white crystals.

(*b*) The salt is only sparingly soluble in water; for example, at 15°C, only 9 g of the salt will dissolve in 100 g of water.

Chemical Properties of Sodium Bicarbonate

(*a*) Sodium bicarbonate in aqueous solution is slightly alkaline in reaction owing to hydrolysis, thus—

$$NaHCO_3 \rightleftharpoons Na^+ + HCO_3'$$

$$H_2O \rightleftharpoons H^+ + OH'$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3'$$

Thus, sodium bicarbonate provides the interesting example of an acid salt which in aqueous solution exhibits an alkaline reaction.

(*b*) If the aqueous solution of sodium bicarbonate is heated decomposition occurs as follows—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

Uses of Sodium Bicarbonate. This salt is employed in the manufacture of baking powders, hence the name "baking soda" which is sometimes applied to this compound. It also finds important application for medicinal purposes, for example the correction of stomach acidity.

Sodium Sesquicarbonate, $Na_2CO_3 . NaHCO_3 . 2H_2O$. This compound is a white crystalline solid formed by allowing a solution containing equimolecular proportions of sodium carbonate and sodium bicarbonate to crystallize above 35°C. Sodium sesquicarbonate is sometimes known commercially as "concentrated soda crystals."

This compound is neither deliquescent nor efflorescent and is freely soluble in water. In aqueous solution its reactions are similar to those given by a mixed solution of sodium carbonate and sodium bicarbonate. It finds extensive application for wool scouring.

Sodium Chloride (common salt), NaCl. As stated earlier sodium chloride occurs widely in nature both in the solid state as well as in solution. In the solid state the crystals are colourless and cubic when pure but often naturally occurring specimens are tinted because of the presence of impurities.

The Salt Industry

Sodium chloride is the basic raw material employed for the manufacture of a large number of compounds such as caustic soda, sodium carbonate, sodium sulphate, sodium phosphates, sodium chlorate and hypochlorite, elemental sodium and hydrochloric acid. In addition practically all the world's supply of chlorine is obtained from sodium chloride. It is therefore understandable that the salt industry assumes considerable importance in all parts of the world.

Salt is obtained in the following three ways.

(*a*) By the evaporation of sea water or salt lake water, or by the evaporation and crystallization of brines pumped from wells.

(*b*) By the mining of rock salt.

(*c*) Directly from sea water.

In Great Britain the majority of the salt of commerce is obtained by the evaporation of brine, either that occurring naturally or that prepared by pumping water into deposits of rock salt. In the U.S.A. over half the salt used is obtained by solar evaporation, a large proportion of which comes from the San Fransisco Bay region and the Great Salt Lake of Utah. The purity of salt obtained from rock salt deposits and from brines often runs as high as 99·5 per cent, but the purity of the salt first obtained by the evaporation of salt water is usually about 95 per cent.

Various types of salt are distinguished. For example, "lump salt" is made by boiling down brine in salt pans; rapid evaporation is carried out at 107·7°C (i.e. the boiling point of the solution), and the fine salt which separates is raked to the sides of the pan. Every eight to twelve hours salt is withdrawn from the salt pans, placed in wooden moulds and cooled until the mother liquors crystallize, so binding the whole lump together.

"Table salt" is manufactured either by grinding lump salt, or by

draining the separated fine crystals. To prevent deliquescence in use caused by the presence of magnesium chloride, a small amount of sodium phosphate is added which forms the non-deliquescent magnesium phosphate by double decomposition; or alternatively small quantities (3 per cent) of bran are added to absorb the moisture due to the deliquescing magnesium chloride.

"Fishery salt" and "Manufacturers' salt" are coarse-grained salts formed by slow evaporation of the brine at 30°–60°C. The addition of small amounts of alum favours the production of large crystals. "Bay salt" is a very coarse-grained salt produced by very slow evaporation of the brine at 40°–50°C.

Pure sodium chloride may be prepared in the laboratory by passing hydrogen chloride gas through a saturated solution of the impure salt. In this way the concentration of the Cl′ ion is greatly increased so that by reason of the *common ion effect* (*see* p. 336) pure sodium chloride is precipitated, the impurities being left in solution.

Physical Properties of Sodium Chloride

(*a*) Sodium chloride is a transparent crystalline solid occurring in the form of cubes or octahedra. It possesses a simple cubic lattice of the type described on p. 127.

(*b*) It melts at 801°C, and boils at 1490°C, its vapour having the constitution NaCl.

(*c*) Sodium chloride dissolves in water with absorption of heat. Its solubilities from 0°C to its boiling point at 107·7°C are given below.

TABLE 79

Variation with Temperature of the Solubility of Sodium Chloride

Temperature (°C)	Solubility (g NaCl/100 g water)
0·0	35·63
10·0	35·69
20·0	35·82
40·0	36·32
60·0	37·06
80·0	38·00
100·0	39·12
107·7	39·65

Sodium chloride exists in human blood to the extent of 2·5 per cent.

Chemical Properties of Sodium Chloride

(*a*) Pure sodium chloride is unchanged on exposure to the atmosphere, although impure specimens containing magnesium chloride are hygroscopic.

(*b*) The aqueous solution of sodium chloride is neutral to indicators, since it contains only sodium and chlorine ions by virtue of the electrolytic dissociation which the solute undergoes.

(*c*) Electrolysis of the aqueous solution gives rise to the evolution of chlorine at the anode and hydrogen at the cathode; in addition a high concentration of hydroxyl ions is also produced in the region of the cathode. Under suitable conditions the electrolysis of such aqueous solutions is employed for the manufacture of sodium hydroxide, sodium carbonate, sodium hypochlorite and sodium chlorate.

Electrolysis of the fused salt yields chlorine at the anode and elemental sodium at the cathode.

Uses of Sodium Chloride. Probably the most important use for sodium chloride is as an essential part of the human diet. It is also employed for the seasoning of foods.

Salt also finds important application in the "salt-glazing" of earthenware articles. For this purpose salt is thrown into the furnace in which the earthenware articles are being fired; the salt reacts with the silica in the clay to form a fusible sodium silicate which, on cooling, forms a hard, lustrous surface on the article, the chemical reaction involved being as follows—

$$2NaCl + \underset{\text{Silica, in the clay}}{SiO_2} + H_2O = Na_2SiO_3 + 2HCl$$

Other important uses for sodium chloride include its application in the manufacture of sodium compounds by electrolytic methods as described above, in the manufacture of hydrochloric acid and chlorine in soap manufacture and the manufacture of sodium by Down's process.

Sulphur Compounds of Sodium

Sodium Sulphide, Na_2S. In the laboratory, sodium sulphide may be prepared by passing hydrogen sulphide through a solution of sodium hydroxide, the reactions involved being as follows—

(*a*) $$NaOH + H_2S = NaHS + H_2O$$

(*b*) $$NaHS + NaOH = Na_2S + H_2O$$

On a commercial scale, sodium sulphide is made by heating salt cake (crude sodium sulphate) with coal, thus—

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

Sodium sulphide is extracted from the mass by leaching out with water and the resulting solution evaporated to give $Na_2S \cdot 9H_2O$.

Sodium sulphide finds application in the dyestuffs industry for the manufacture of sulphide dyes, in the extraction of silver and in the tanning industries.

Sodium Bisulphite (Sodium Hydrogen Sulphite), $NaHSO_3$. Sodium bisulphite is made by saturating a solution of caustic soda with sulphur dioxide, thus—

$$NaOH + SO_2 = NaHSO_3$$

On crystallizing, sodium metabisulphite is produced—

$$2NaHSO_3 = Na_2S_2O_5 + H_2O$$

Sodium metabisulphite forms the bisulphite again on being dissolved in water.

Sodium bisulphite is used in large quantities in the manufacture of paper, as an antichlor and disinfectant, and as a constituent of acid fixing solution used in photography.

Sodium Sulphite, Na_2SO_3. The normal salt, sodium sulphite, is made by adding an equivalent quantity of sodium hydroxide to a solution of sodium bisulphate. The reaction involved is as follows—

$$NaHSO_3 + NaOH = Na_2SO_3 + H_2O$$

On a large scale this compound is prepared by passing sulphur dioxide over crystals of washing soda--

$$Na_2CO_3 \cdot 10H_2O + SO_2 = Na_2SO_3 + CO_2 + 10H_2O$$

Sodium Bisulphate (Sodium Hydrogen Sulphate), $NaHSO_4$. Sodium bisulphate is made on a large scale by the Leblanc process in which salt is heated with sulphuric acid.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

It is also manufactured under the name of "nitre cake" as a by-product of the manufacture of nitric acid when sodium nitrate is heated with sulphuric acid—

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

On heating sodium bisulphate it first decomposes with the formation of sodium pyrosulphate, thus—

$$2NaHSO_4 = Na_2S_2O_7 + H_2O$$

On further heating, at red heat, sodium sulphate and sulphur trioxide are formed—

$$Na_2S_2O_7 = Na_2SO_4 + SO_3$$

Sodium bisulphate may be used as a substitute for sulphuric acid as it contains a replaceable hydrogen atom; in this connexion it finds application for the pickling of rolled mild steel plates prior to hot tinning, and for the production of carbon dioxide from naturally occurring carbonates such as limestone and dolomite. In the laboratory, sodium bisulphate is used in chemical analysis for opening up refractory minerals.

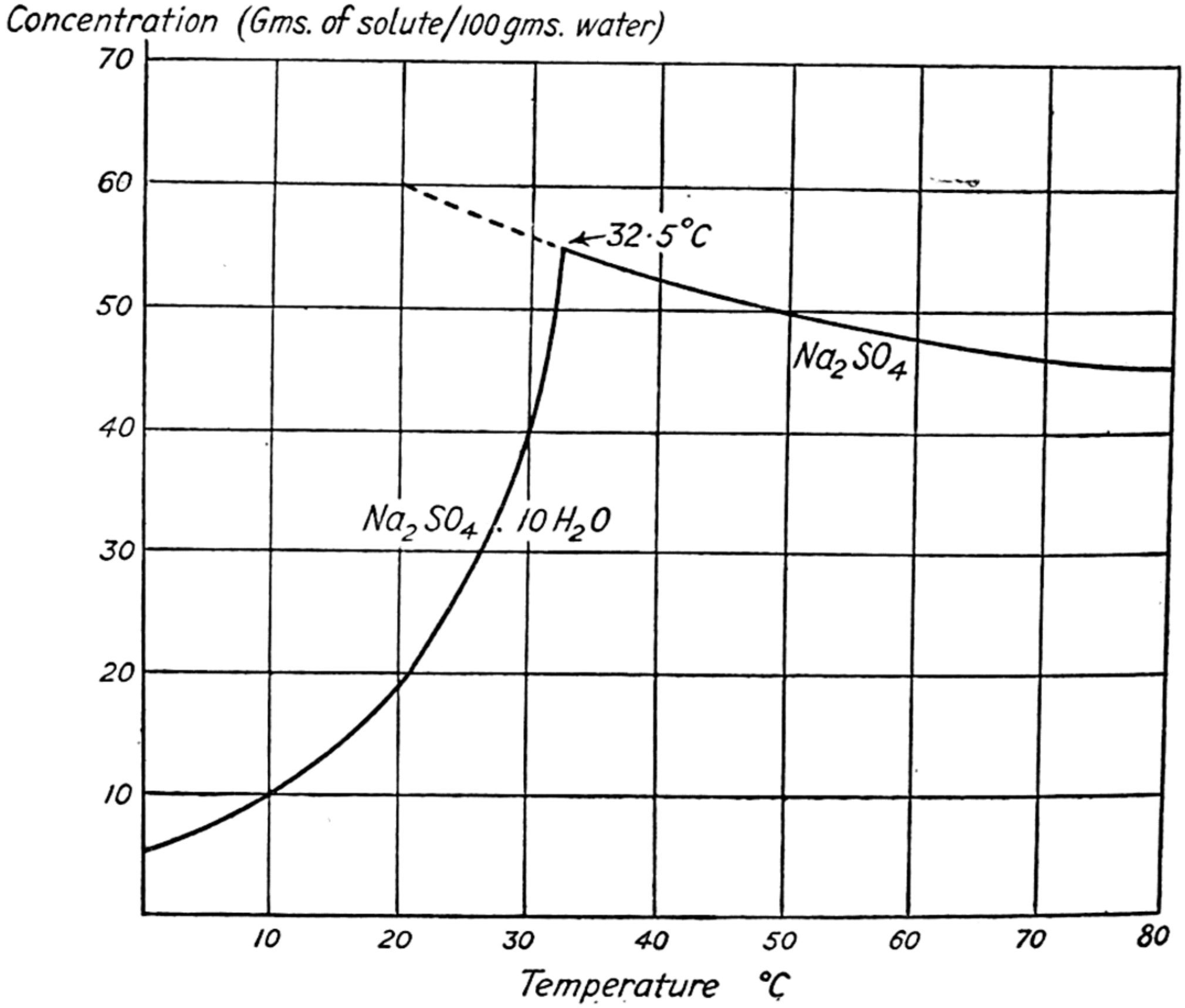


FIG. 159. Solubility Curve for Sodium Sulphate

Sodium Sulphate (Salt Cake), Na_2SO_4. Sodium sulphate is manufactured by the Leblanc process. Sulphuric acid reacts with salt in two stages as follows—

(*a*) $NaCl + H_2SO_4 = NaHSO_4 + HCl$

(*b*) $NaCl + NaHSO_4 = Na_2SO_4 + HCl$

Sodium sulphate is readily soluble in water, the form of the solubility curve being shown in Fig. 159. Below 32·5°C, the salt crystallizes in the form of large monoclinic prisms as the decahydrate, $Na_2SO_4 . 10H_2O$, which is known as "Glauber's salt." Sodium sulphate readily exhibits the phenomenon of supersaturation (*see* p. 134). Thus if a hot, concentrated solution of this salt is allowed to cool to the temperature of the

atmosphere without the admission of dust or forcing matter and without disturbance, no crystals will be formed; but if a crystal of the decahydrate then be dropped into the supersaturated solution there will be an immediate crystallization with the evolution of considerable heat. If the supersaturated solution is cooled to 5°C, the crystals which separate are those of the heptahydrate, $Na_2SO_4 . 7H_2O$.

Sodium sulphate in the anhydrous condition is employed in the manufacture of glass. It also has medicinal uses, and constitutes a source of sodium sulphide.

Sodium Thiosulphate (Photographic Hypo) $Na_2S_2O_3$. Sodium thiosulphate is made on a large scale from "alkali waste," that is, calcium sulphide, CaS. When air is blown through a suspension of the sulphide in water calcium thiosulphate is formed and on reaction with either sodium carbonate or sodium sulphate, sodium thiosulphate is produced, which remains in solution and either calcium carbonate or calcium sulphate is precipitated.

$$CaS_2O_3 + Na_2SO_4 = CaCO_3 \downarrow + Na_2S_2O_3$$
$$CaS_2O_3 + Na_2CO_3 = CaSO_4 \downarrow + Na_2S_2O_3$$

Sodium thiosulphate reacts with acids to give a slowly precipitated deposit of sulphur—

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + SO_2 \uparrow + S \downarrow$$

This reaction should be compared with the following—

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2 \uparrow$$

The deposition of sulphur in the case of the thiosulphate affords a means of distinguishing it from the sulphite.

Sodium thiosulphate reacts with iodine to give sodium tetrathionate, thus—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

This reaction is employed in analytical chemistry in the case of those reactions in which iodine is liberated.

Sodium thiosulphate reacts with many salts which are insoluble in water to form complex salts, e.g.—

$$Na_2S_2O_3 + AgCl = Na[AgS_2O_3] + NaCl$$

This particular reaction is employed in photography as a means of *fixing* those portions of a photographic emulsion which have not been exposed to the light. The portions of the emulsion exposed to light in the camera suffer reduction, at first in the camera, and later, in the developer. This reduction leads to the liberation in these regions of metallic silver which of course is unaffected by the "solvent" action of the sodium thiosulphate as depicted in the above chemical equation.

Nitrogen Compounds of Sodium

Sodium Nitrate (Chile Saltpetre or Caliche), $NaNO_3$. Immense deposits of crude sodium nitrate are found in the desert regions on the borders of Chile and Peru. This crude *caliche* contains approximately 65 per cent sodium nitrate, 2–15 per cent potassium nitrate, up to 20 per cent of sodium chloride and smaller amounts of sodium iodate, sodium chlorate, sodium perchlorate and gypsum.

The caliche is crushed and then dissolved in water. The clear liquor is run off and allowed to stand for several days during which time most of the nitrate is deposited. The mother liquor is then worked up for its iodine content.

Sodium nitrate is a white, crystalline solid which is very soluble in water. When heated, the salt melts at 316°C, and at high temperatures it decomposes, forming sodium nitrite and liberating oxygen, thus—

$$2NaNO_3 = 2NaNO_2 + O_2$$

Sodium nitrate is used as a fertilizer and in the manufacture of potassium nitrate and sodium nitrite.

Sodium Nitrite, $NaNO_2$. Sodium nitrite may be made either by heating sodium nitrate, as described above, or alternatively by heating sodium nitrate with lead, when the following reaction occurs—

$$NaNO_3 + Pb = NaNO_2 + PbO$$

The sodium nitrite is extracted by leaching out with water, the litharge being left behind as an insoluble sludge.

The chief use of this compound is in the manufacture of azo dyestuffs.

POTASSIUM

Occurrence. Potassium is much too reactive to occur free in nature. It is however widely distributed in the earth's crust; the chief forms in which it occurs are detailed below.

Felspars and Related Minerals. The chief of these minerals are—

Orthoclase felspar	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$
Leucite	$K_2O \cdot Al_2O_3 \cdot 2SiO_2$
Muscovite or potash mica	$2H_2O \cdot K_2O \cdot 2Al_2O_3 \cdot 6SiO_2$

On weathering, these igneous rocks give the carbonate which, being soluble in water, is leached out by rain and spring water. This potassium carbonate reacts with complex minerals such as the zeolites in a manner of which the following is typical—

$$Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O + K_2CO_3 = K_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O + Na_2CO_3$$

The potassium is therefore largely retained in the soil, and it is because of this fact that potassium salts constitute a smaller proportion of the total solids found in lake and sea waters than those of sodium.

Salt Deposits. The intensive evaporation of vast inland seas in prehistoric times has led to the formation of salt deposits which contain potassium salts along with salts of other metals. The most important deposit of this kind is that of Stassfürt in Germany, and in this deposit the most important potassium compound is *carnallite*, $KCl . MgCl_2 . 6H_2O$; other potassium minerals found in the Stassfürt salt deposits include *kainite*, $KCl . MgSO_4 . 2CaSO_4 . 2H_2O$, *polyhalite*, $K_2SO_4 . MgSO_4 . 2CaSO_4 . 2H_2O$, and *sylvine*, KCl.

Another potassium mineral occurring in the form of a salt deposit is *alunite*, $K_2O . 3Al_2O_3 . 4SiO_3 . 6H_2O$, which is found in seams and pockets in widely separated localities from New South Wales to Nevada and Italy.

Nitre, KNO_3, occurs in the Chilean deposits of caliche.

Sea Water. Sea water contains about 0·04 per cent of potassium salts and the recovery of such salts supplies a small proportion of the potash production. In a similar way the waters of salt lakes such as the Dead Sea and Searles Lake in California have been worked in recent years for potassium salts, etc.

The mineral *glauconite*, a hydrated silicate of iron and potassium originally deposited on the beds of prehistoric oceans and now found extensively in the chalk marl and greensand of the cretacious rocks in England and elsewhere, has also been worked on a small scale for its potash content.

Organic Potassium Compounds. All plants contain a certain proportion of potassium, derived originally from the soil. The potassium occurs in the plants in the form of potassium salts of organic acids. Thus, potassium hydrogen tartrate, $KHC_4H_4O_6$, occurs as "argol" or "cream of tartar" in grape juice, and potassium hydrogen oxalate, KHC_2O_4, in rhubarb and sorrel. That potassium compounds are present in plants is demonstrated by the fact that plant ashes consist to a large extent of potassium carbonate or potash.

Extraction of Potassium. Potassium is extracted by electrolytic methods similar to those employed for the extraction of sodium (*see* p. 422). In general the Downs's process is to be preferred owing to the comparatively high solubility of metallic potassium in fused caustic potash.

Properties of Potassium. Potassium is very similar in properties to sodium, except that in chemical reactions it usually reacts in a more violent manner. Thus, potassium exhibits a very great affinity for the electronegative elements such as the halogens, oxygen and sulphur. It combines directly with hydrogen when heated to about 350°C, to form the hydride.

In a similar manner to sodium, potassium forms potassamide, KNH_2, when heated in gaseous ammonia and dissolves in liquid ammonia to form a blue colloidal solution. It also dissolves in mercury to form potassium amalgam.

When heated in air, potassium burns and ultimately forms potassium tetroxide, K_2O_4.

Uses of Potassium. Potassium is not so widely used in industry as is sodium. It is used, however, in small quantities, for the manufacture of certain types of photocells.

Compounds of Potassium

Potassium Hydroxide (Caustic Potash), KOH. Potassium hydroxide is made by methods similar to those employed for preparing caustic soda. In its physical and chemical properties caustic potash closely resembles caustic soda. Its solubility both in water and in ethyl alcohol however is higher than that of caustic soda. In addition potassium hydroxide is more hygroscopic than sodium hydroxide, and further, in the case of the former compound, no incrustation of dry carbonate forms on the surface after exposure to the atmosphere since potassium carbonate is soluble in concentrated potassium hydroxide solution. These facts make for the utilization of caustic potash as an absorbent for carbon dioxide in preference to sodium hydroxide.

Uses of Potassium Hydroxide. In addition to the utilization of potassium hydroxide solution in the laboratory as an absorbent for carbon dioxide, it also finds application for the manufacture of soft soap—a mixture of potassium oleate, stearate and palmitate. Caustic soda is used for the making of hard soap, composed of the corresponding sodium salts of the fatty acid radicals just quoted.

Potassium Carbonate (Potash or Pearl Ash) K_2CO_3. Potassium carbonate was formerly obtained from wood ashes which were leached with water and the crude potassium carbonate obtained by evaporation of the resulting solution in large pots (hence the term "pot-ash"). On recrystallization a purer product may be obtained which possesses a pearly appearance (hence the term "pearl ash").

The Magnesia Process. At the present time the majority of the potassium carbonate of commerce is made by "Precht's process" or the "Magnesia process." It should be noted that the Solvay process cannot be used since potassium bicarbonate is much more soluble in water than is sodium bicarbonate and the former would not separate out as a sludge in the carbonating towers as does sodium bicarbonate.

The success of the Magnesia process depends upon the comparative insolubility of the double carbonate of potassium and magnesium, $KHCO_3 . MgCO_3 . 4H_2O$.

In the Magnesia process carbon dioxide is passed through a suspension

of hydrated magnesium carbonate in a concentrated solution of potassium chloride, when the insoluble double carbonate is precipitated thus—

$$3[MgCO_3 . 3H_2O] + 2KCl + CO_2 = 2[KHCO_3 . MgCO_3 . 4H_2O] \downarrow + MgCl_2$$

The double carbonate is filtered off from the solution and then either treated with water under pressure when the following reaction occurs—

$$2KHCO_3 . MgCO_3 . 4H_2O = 2MgCO_3 \downarrow + K_2CO_3 + 9H_2O + CO_2$$

or, alternatively, the precipitate is treated with a suspension of magnesium oxide in water below 20°C, when the following reaction takes place—

$$2KHCO_3 . MgCO_3 . 4H_2O + MgO = 2MgCO_3 . 3H_2O \downarrow + K_2CO_3$$

In either case the hydrated magnesium carbonate is filtered off and the potassium carbonate crystallized from the filtrate. Since sodium carbonate does not form a double carbonate with magnesium carbonate under the conditions which obtain, there is no contamination of the resulting potassium carbonate with the corresponding sodium salt.

In the laboratory pure potassium carbonate may be obtained either by heating potassium bicarbonate—

$$2KHCO_2 = K_2CO_3 + H_2O + CO_2$$

or alternatively, by heating potassium hydrogen tartrate in the air—

$$2KHC_4H_4O_6 + 5O_2 = K_2CO_3 + 5H_2O + 7CO_2$$

Properties of Potassium Carbonate. Potassium carbonate is a white deliquescent powder which is freely soluble in water. Potassium carbonate crystallizes from solution at temperatures of 10°–25°C, as the trihydrate, $K_2CO_3 . 3H_2O$. At 100°C the trihydrate loses two molecules of water of crystallization and at 130°C, it becomes anhydrous. In aqueous solution potassium carbonate suffers hydrolysis and its solution therefore gives an alkaline reaction.

Uses of Potassium Carbonate. Potassium carbonate is used in the manufacture of hard glass, in the manufacture of soft soap, in the dye-stuffs industry and as the starting material for the preparation of many potassium compounds.

Potassium Bicarbonate, $KHCO_3$. Potassium bicarbonate is made either by passing carbon dioxide through a cold, concentrated solution of potassium carbonate, or alternatively by passing carbon dioxide over moist potassium carbonate. In the former case the salt separates out as a precipitate which is then filtered off and dried; in the latter case the product is dried on a porous plate.

Potassium bicarbonate is about three times as soluble as sodium carbonate under the same conditions. The aqueous solution of potassium bicarbonate is strongly alkaline owing to hydrolysis.

Potassium Chloride, KCl. Potassium chloride occurs naturally as sylvine, and this source of supply is augmented by extracting it from carnallite. It is extracted from this latter mineral by dissolving it in water and then chilling the solution, when the potassium chloride separates out leaving the magnesium chloride in solution. The mother liquor remaining behind after the removal of the potassium chloride is used again for treating a further quantity of carnallite.

In very many ways potassium chloride is similar to sodium chloride. In spite of these chemical similarities, however, these two chlorides are different in their physiological action, thus potassium chloride cannot be substituted for sodium chloride in the human diet.

Potassium chloride is used extensively as a fertilizer and as a raw material for the manufacture of other potassium compounds.

Potassium Bromide, KBr. On a large scale potassium bromide is made by acting on iron borings with bromine so forming iron bromide, thus—

$$4Br_2 + 3Fe = Fe_3Br_8$$

This ferroso-ferric bromide is then caused to react with an aqueous solution of potassium carbonate when ferrous and ferric hydroxides are precipitated and potassium bromide remains in solution, thus—

$$Fe_3Br_8 + 4K_2CO_3 + 4H_2O = 8KBr + 2Fe(OH)_3\downarrow + Fe(OH)_2\downarrow + 4CO_2$$

The solution of potassium bromide is filtered off and the salt crystallized out.

Alternatively potassium bromide may be prepared by the action of bromine on heated potassium hydroxide solution. The following reaction occurs—

$$6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O$$

The solution of potassium bromide and potassium bromate is evaporated to dryness and the potassium bromate reduced to the bromide by heating the residue with charcoal when the following reaction occurs—

$$2KBrO_3 + 3C = 2KBr + 3CO_2$$

Potassium bromide occurs in the form of transparent crystals exhibiting a cubic form; it is very soluble in water.

Potassium bromide finds application in photography and also for medicinal purposes.

Potassium Iodide, KI. Potassium iodide is prepared from potassium carbonate and ferroso-ferric iodide by methods closely parallel to those employed for the manufacture of potassium bromide. Similarly it may also be prepared by the action of iodine on hot concentrated potassium carbonate solution.

Properties of Potassium Iodide

(*a*) An aqueous solution of potassium iodide dissolves iodine, forming potassium tri-iodide, KI_3, in the process. This solution of potassium tri-iodide in water gives all the reactions of free, elemental iodine and for the purposes of practical chemistry may be regarded as a simple solution of the element in potassium iodide solution.

(*b*) Potassium iodide reacts with many metallic salts to form insoluble iodide, thus—

$$2CuSO_4 + 4KI = Cu_2I_2\downarrow + I_2\downarrow + 2K_2SO_4$$

This particular reaction forms the basis for the determination of the copper content of copper-base alloys, etc., since one gramme atomic weight of iodine is liberated by each gramme atomic weight of copper; the amount of iodine is capable of ready determination by titration with sodium thiosulphate solution, the end-point being shown by the removal of the blue colour which iodine gives on reaction with starch. The reaction involved in the sodium thiosulphate titration is as follows—

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

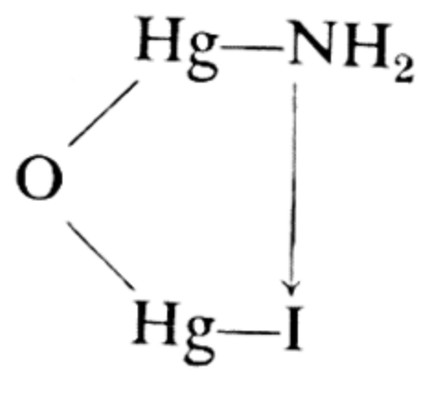
Another iodide capable of precipitation from its aqueous solutions is mercuric iodide—

$$HgCl_2 + 2KI = HgI_2\downarrow + 2KCl$$

With excess of potassium iodide, however, the mercuric iodide dissolves to form a complex potassium mercuri-iodide, as follows—

$$HgI_2 + 2KI = K_2[HgI_4]$$

A solution of potassium mercuri-iodide rendered strongly alkaline with sodium hydroxide is known as *Nessler's solution*. The presence of a trace of ammonia, or of an ammonium salt, produces a yellow solution of the iodide of *Millon's base*,



The presence of a larger amount of ammonia produces a brown precipitate.

(*c*) The aqueous solution of potassium iodide is neutral to indicators.

(*d*) If an acid is added to potassium iodide solution hydriodic acid is formed and the solution therefore exhibits reducing properties. This fact is of value in chemical analysis since iodine may be liberated by oxidizing agents, the amount liberated being a measure of the amount of oxidizing agent used. The liberated iodine is readily determined by

titration with sodium thiosulphate solution as described above. The following reactions will serve to illustrate this point.

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$
$$2KMnO_4 + 10KI + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$
$$H_2O_2 + 2KI + H_2SO_4 = K_2SO_4 + 2H_2O + I_2$$
$$CaOCl_2 + 2KI + 2HCl = CaCl_2 + 2KCl + H_2O + I_2$$

Potassium Sulphate, K_2SO_4. Potassium sulphate may be manufactured in the same way as sodium sulphate. On a large scale, however, it is generally obtained from such minerals as *schönite*, $K_2SO_4 . MgSO_4 . 6H_2O$, by a process of fractional crystallization.

In contrast to sodium sulphate, potassium sulphate crystallizes from aqueous solution in the form of anhydrous rhombic crystals. It is also much less soluble in water than the sodium salt. The chief use for potassium sulphate is as a fertilizer, for which purpose it is used in tremendous quantities.

Potassium Bisulphate (Potassium Hydrogen Sulphate), $KHSO_4$. Potassium bisulphate closely resembles the corresponding sodium salt. It finds application in chemical analysis for "opening up" refractory metallic oxides which are not readily dissolved by the usual acids. Platinum crucibles and basins are readily cleaned by fusing a little of the salt within them and then dissolving out the residue with water.

Potassium Nitrate (Saltpetre or Nitre), KNO_3. Potassium nitrate occurs as a saline efflorescence, probably of organic origin, on the surface of the soil in parts of Central India. Other deposits of this nitre or saltpetre are found in South Africa and in Brazil. The nitre may be extracted by leaching with water.

Manufacture of Potassium Nitrate. On a commercial scale potassium nitrate is made by the reaction of potassium chloride with sodium nitrate, thus—

$$KCl + NaNO_3 = KNO_3 + NaCl$$

In the resulting solution there are present four ions, namely, K^+, Na^+, NO_3', and Cl'. On evaporation the least soluble salt capable of being formed from these ions separates out first; this salt is sodium chloride. Accordingly, the sodium chloride is filtered off and the solution cooled further when the potassium nitrate crystallizes out.

Properties of Potassium Nitrate. In its properties potassium nitrate is very similar to sodium nitrate. It is however not deliquescent like sodium nitrate and hence is used in the manufacture of gunpowder (75 per cent potassium nitrate, 15 per cent carbon, and 10 per cent sulphur).

Uses of Potassium Nitrate. The chief uses of potassium nitrate are as a fertilizer, for the pickling of meat, for medicinal purposes and as a constituent of gunpowder.

THE COINAGE METALS

Group I*b* of the Periodic Table is composed of three metals—copper, silver and gold. All three of these metals occur native and form a natural group. They have been employed for currency purposes since earliest times, probably because they occur native. They are therefore sometimes referred to as the "Coinage Metals."

Although copper, silver and gold are placed in Group I of the Periodic Table, they have very little in common with the Alkali Metals of Group I*a*, except perhaps their common ability to form colourless, monovalent compounds. It is more satisfactory, therefore, to regard these three metals as members of the three transition series—Scandium-Zinc, Yttrium-Cadmium, and Lanthanum-Mercury. In this group all the members are capable of exerting a valency higher than one and in such cases they form coloured salts.

Copper, silver and gold all exhibit characteristic metallic lustre, they are capable of taking a high polish and show resistance to atmospheric corrosion. All three metals are very malleable and ductile and are excellent conductors of heat and electricity. Copper, silver and gold may all be precipitated from aqueous solutions of their salts by less noble metals such as zinc, aluminium and iron.

All are attacked by chlorine. Only copper is attacked by oxygen directly; the oxides of silver and gold have to be prepared indirectly; these latter two oxides are decomposed readily by heat.

TABLE 80

Some Physical Properties of the Coinage Metals

Property	Copper Cu	Silver Ag	Gold Au
Atomic number	29	47	79
Electronic configuration	2, 8, 18, 1	2, 8, 18, 18, 1	2, 8, 18, 32, 18, 1
Atomic weight	63·54	107·88	197·2
Density (g/cm³ at 20°C)	8·94	10·5	19·3
Atomic volume (cm³/g atom)	7·11	10·27	10·22
Melting point (°C)	1083·0	960·6	1063·0
Boiling point (°C) (760 mm pressure)	2595·0	2001·0	2966·0
Thermal conductivity (cal/cm²/sec at 20°C)	0·923	0·974	0·7072
Electrical resistivity (microhm-cm)	1·682	1·62	2·42
Normal electrode potential (Hydrogen scale)	+ 0·3448v (Cu/Cu″)	+ 0·7995v (Ag/Ag′)	+ 1·42v (Au/Au‴)

None of the three metals will displace hydrogen from acids. Oxidizing acids will attack copper and silver. Some of the more important physical characteristics of copper, silver and gold are given in Table 80 on p. 451.

All these three metals crystallize in the face-centred cubic system.

Copper, silver and gold are all capable of forming two types of compounds, namely—

(i) Monovalent (*-ous*) compounds in which the metal uses the single electron present in the outermost electron shell for the purpose of valency linkage; and

(ii) Polyvalent (*-ic*) compounds in which copper and silver use two electrons and gold three electrons for forming the valency links. In these polyvalent compounds the electrons involved are the single electron present in the outermost electron shell, together with either one or two, as the case may be, in the shell immediately below the outermost shell.

Atoms of these three metals when existing in the monovalent state therefore possess completed electron shells and are thus colourless.

On the other hand when these metals exist in the polyvalent state they possess incomplete penultimate shells with either 16 or 17 electrons; such compounds are coloured. Thus cupric compounds are blue, argentic compounds (e.g. AgF_2) are yellow, whilst auric compounds are brown.

The simple compounds of copper, silver and gold tend to be covalent rather than electrovalent. Thus the vapour of cuprous chloride is bimolecular and therefore covalent. Likewise, argentous chloride and cuprous chloride in the crystalline state possess non-ionic space lattices.

These three metals readily form complex anions and cations. Examples of these complexes will be described under the individual metals.

COPPER

Occurrence. Copper is found native in nature and also in minerals in igneous, sedimentary and in metamorphic rocks. In the Lake Superior district of the U.S.A. native copper is found in steam holes and small fissures in lava flows, as the cementing material between pebbles of a conglomerate, and as replacements in beds of volcanic ash. These deposits give rise to the so-called "lake" copper. Many copper deposits, however, average less than 1 per cent of copper, but such deposits are considered readily and profitably workable when large tonnages of ore are easily accessible. Large-scale mining methods are capable of handling thousands of tons of ore per day. The chief ores of copper are as follows—

Metal	Native copper
Oxide	Cuprite, Cu_2O

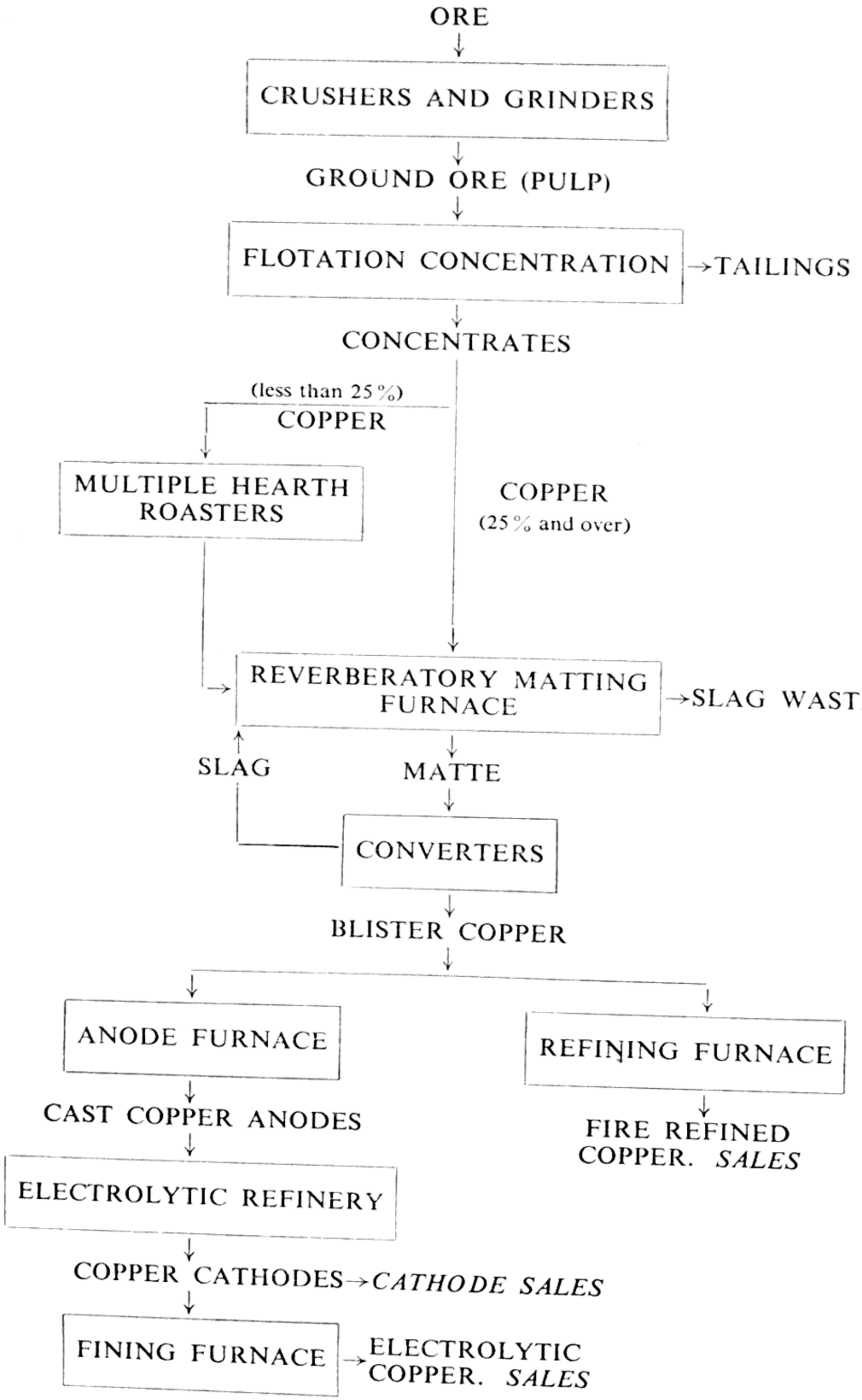


FIG. 160. Flow Sheet for Extraction of Copper

Sulphides	Chalcopyrite or Copper pyrites, $CuFeS_2$; Bornite or Erubescite, Cu_3FeS_3; Chalcocite or Copper glance, Cu_2S
Sulphate	Brochantite, $CuSO_4 . 3Cu(OH)_2$
Carbonates	Malachite, $CuCO_3 . Cu(OH)_2$; Azurite, $2CuCO_3 . Cu(OH)_2$
Silicate	Chrysocolla, $CuO . SiO_2 . 2H_2O$
Chloride	Atacamite, $CuCl_2 . 3Cu(OH)_2$

The U.S.A. has been the world's chief copper-producing country for more than 50 years. Sulphide ores are mined in Utah, Nevada and Montana in the U.S.A., and Northern Rhodesia, the Belgian Congo, and in New South Wales. Carbonate, sulphate and silicate ores are also mined in the Katanga region of the Belgian Congo and in Northern Rhodesia. The sulphate and chloride ores are worked at Chuquicamata, the largest copper-producing mine in the world.

Ores such as those detailed above are always associated with large quantities of non-metal-bearing material which is termed *gangue*, so that although formulae are quoted for the minerals described it should not be imagined that the whole deposit is composed of, say chalcopyrite. In actual fact the average copper content of all copper ore production is not more than 2 per cent. It will, therefore, be appreciated that the ore bodies in Northern Rhodesia averaging 4·11 per cent copper and those in the Katanga region averaging 7 per cent copper are considered very rich deposits indeed.

The Extraction of Copper from Sulphide Ores

The actual methods employed for the extraction of the metal from sulphide ores of high copper content differ in minor detail from plant to plant. In general, however, the following constitute the various stages of the extraction process, the general scheme being shown in Fig. 160.

Flotation. The ore is first crushed to a fine powder after which the mineral particles are separated from those of the gangue by means of the *flotation* process. The principle of the flotation process is that the pulverized ore is fed into a flotation cell in which water and frothing agents such as pine oil and xanthates are maintained in a condition of violent agitation. The mineral particles are "wetted" by the froth and are carried over a weir and thus separated from the gangue particles which are not wetted and so remain behind in the flotation cell. In this way the ore is concentrated. For example, it is possible to obtain a 90 per cent recovery of copper mineral from the ore whilst the concentrate produced has only about 1/15 of the original bulk.

Roasting. The concentrate from the flotation process is then roasted to remove "volatiles" such as arsenic which is removed as As_2O_3, sulphur as SO_2, and antimony as Sb_2O_3.

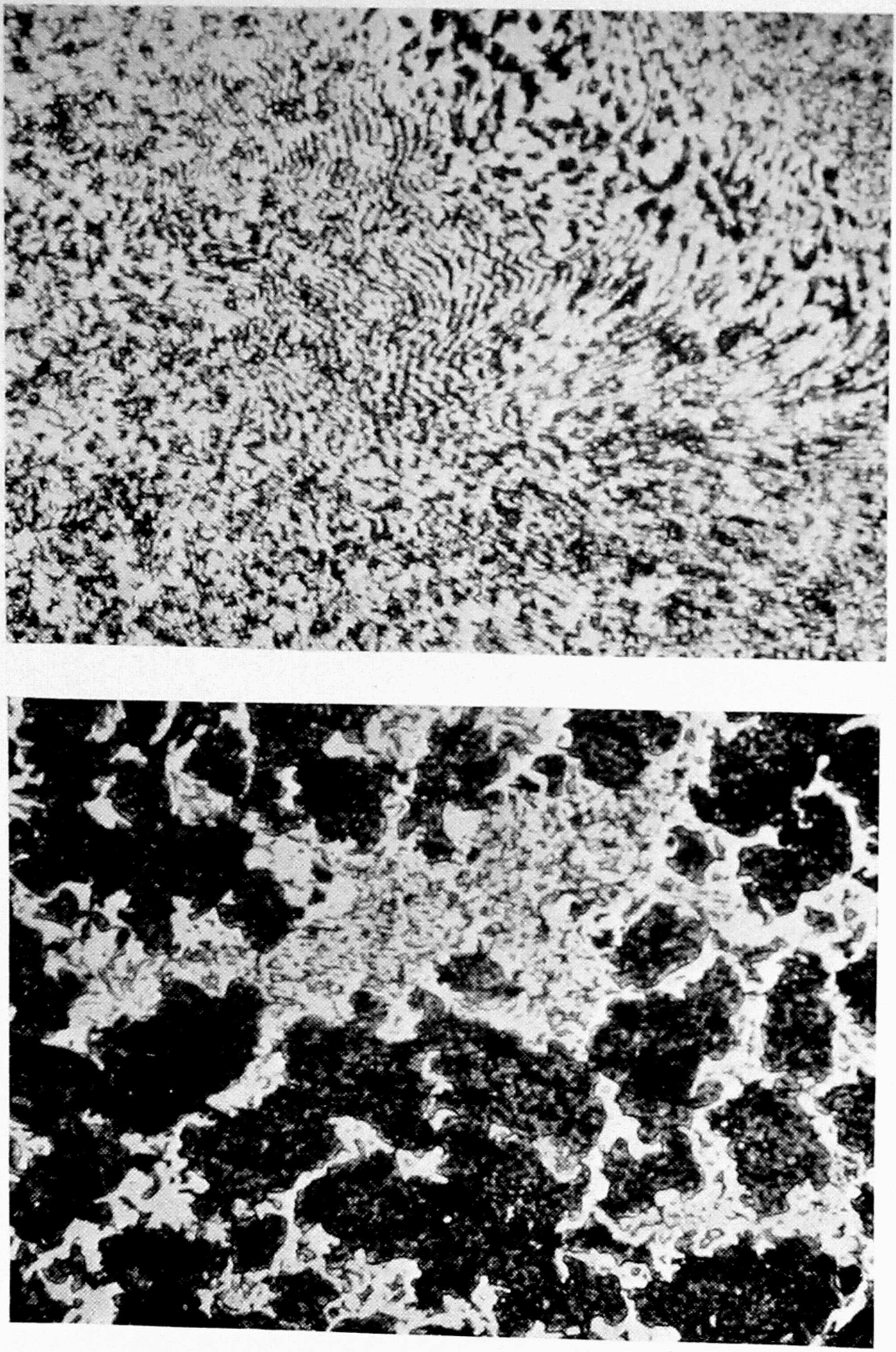
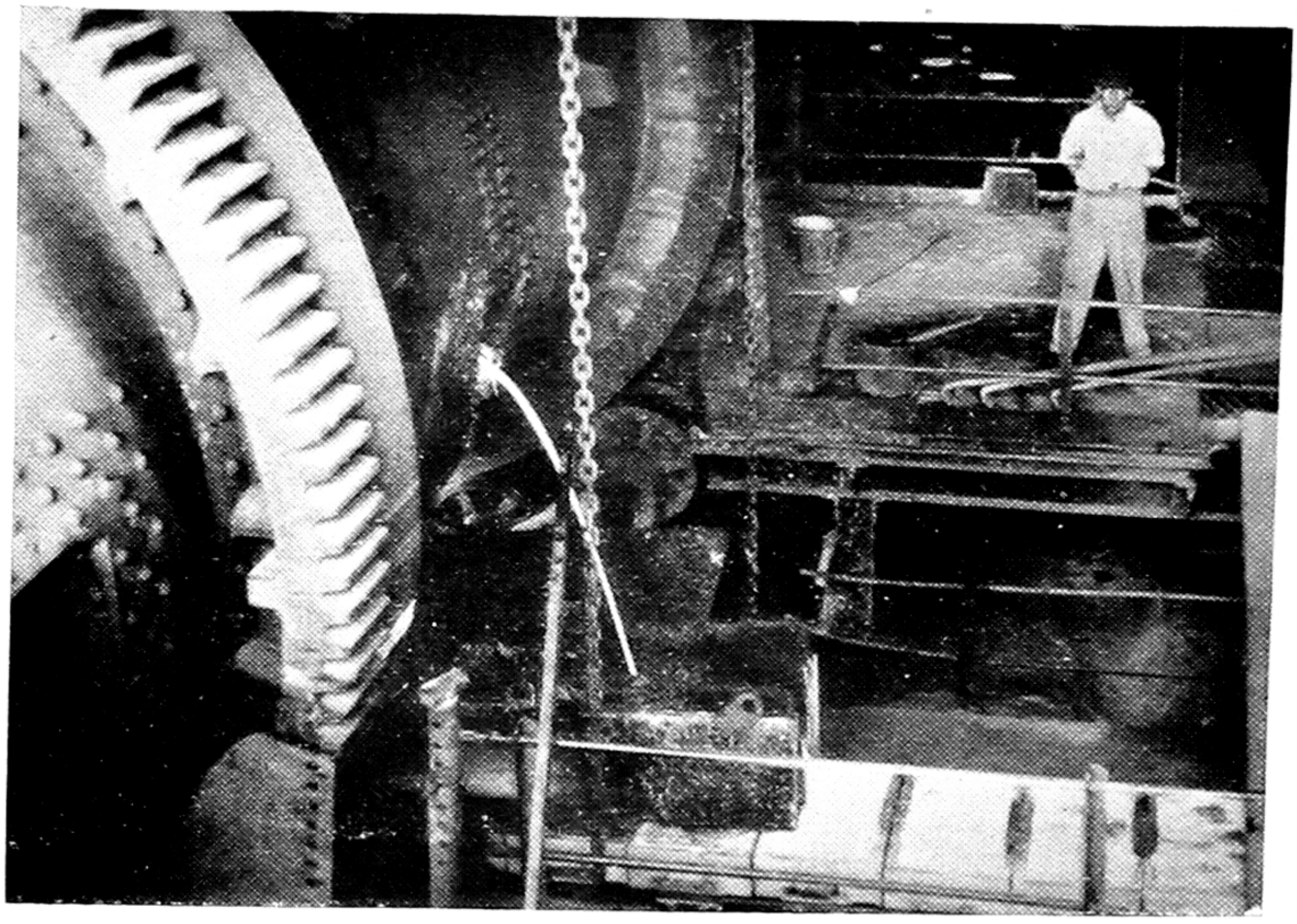


PLATE I

(*Top*) Microstructure of Tinman's Solder (× 250)
(*Bottom*) Microstructure of Plumber's Solder (× 250)

(T.447)



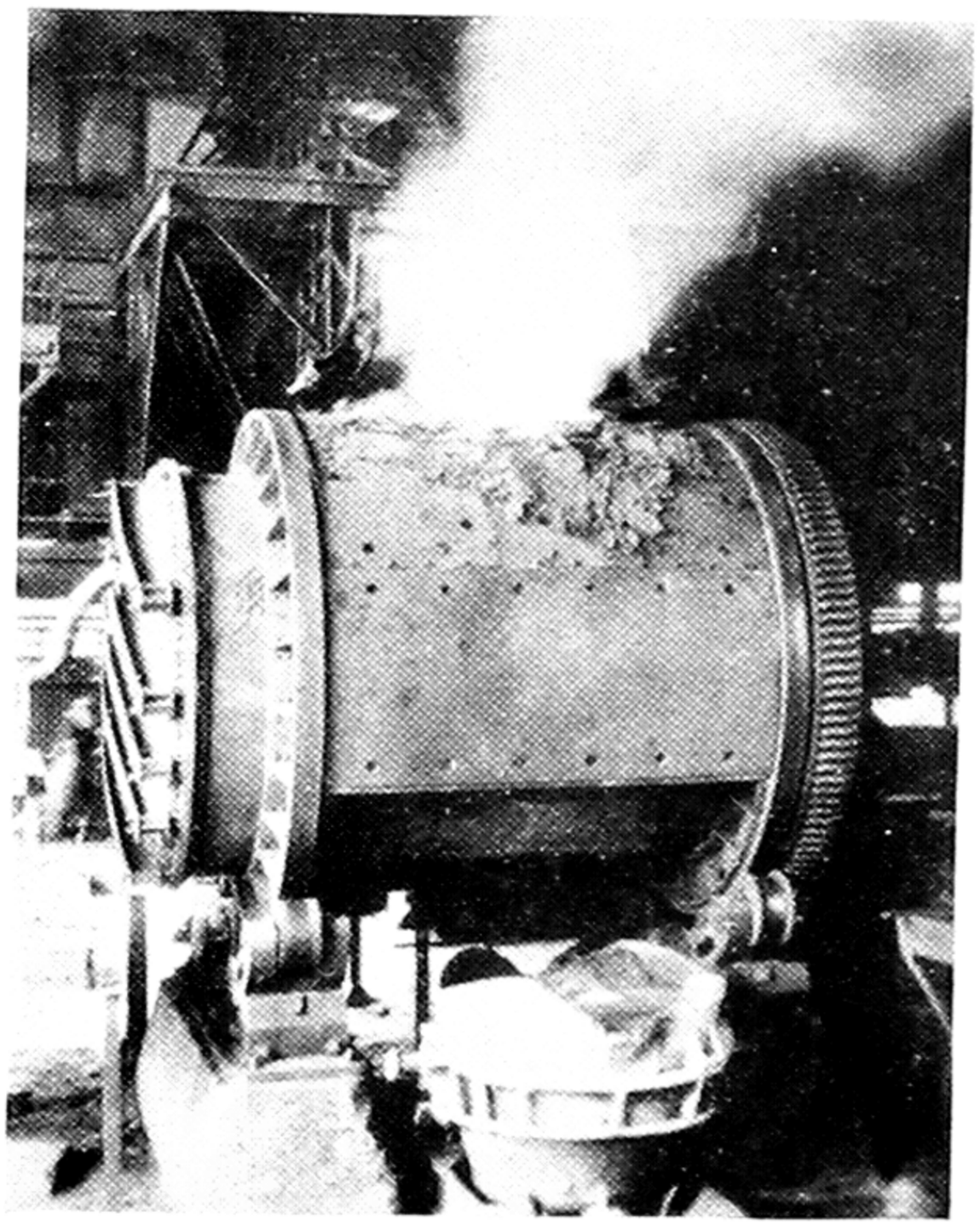


Plate II

(*Top*) Smelter—Casting Blister Copper

(Courtesy of Roan Antelope Copper Mines, Ltd.)

(*Left*) Smelter—Blowing Converter

(Courtesy of Roan Antelope Copper Mines, Ltd.)

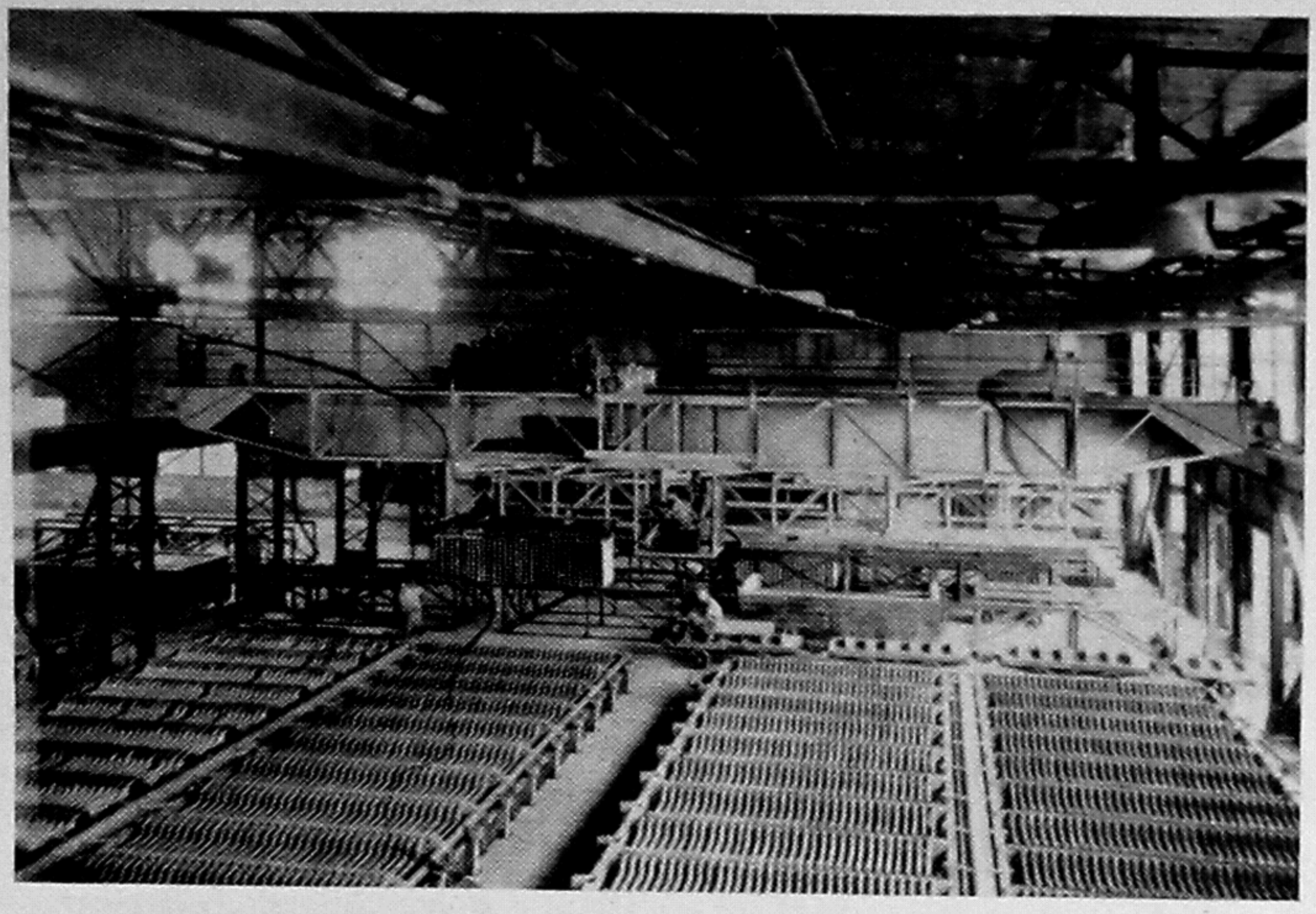


Plate III

(*Top*) Electrolytic Refinery—Interior View of Tank House

(*Courtesy of Rhokana Corporation, Ltd.*)

(*Right*) Poling in the Fire Refinery

(*Courtesy of Enfield Copper Refining Company, Ltd.*)

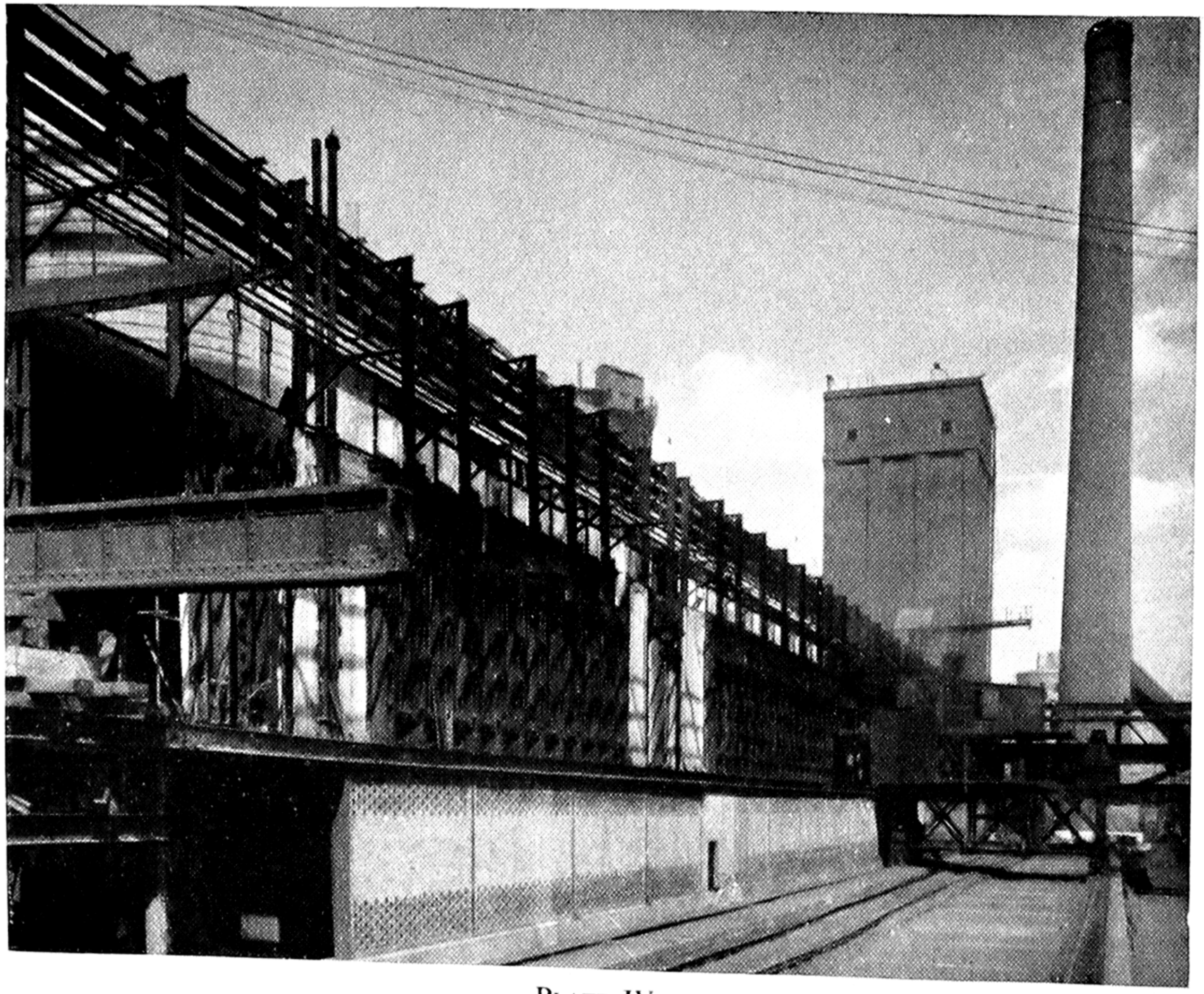


PLATE IV

Becker Coke Ovens—Ram Side

(Courtesy of Guest Keen Baldwins Iron and Steel Co., Ltd.)

This roasting is usually carried out in a mechanically-charged multi-floor furnace (*see* Fig. 161). The chief reaction involved is as follows—

$$2CuFeS_2 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$

Smelting. The roasted ore is then transferred to a reverberatory furnace (*see* Fig. 162) along with sand to act as a flux and smelted in a non-oxidizing atmosphere. Under these conditions the iron oxide reacts

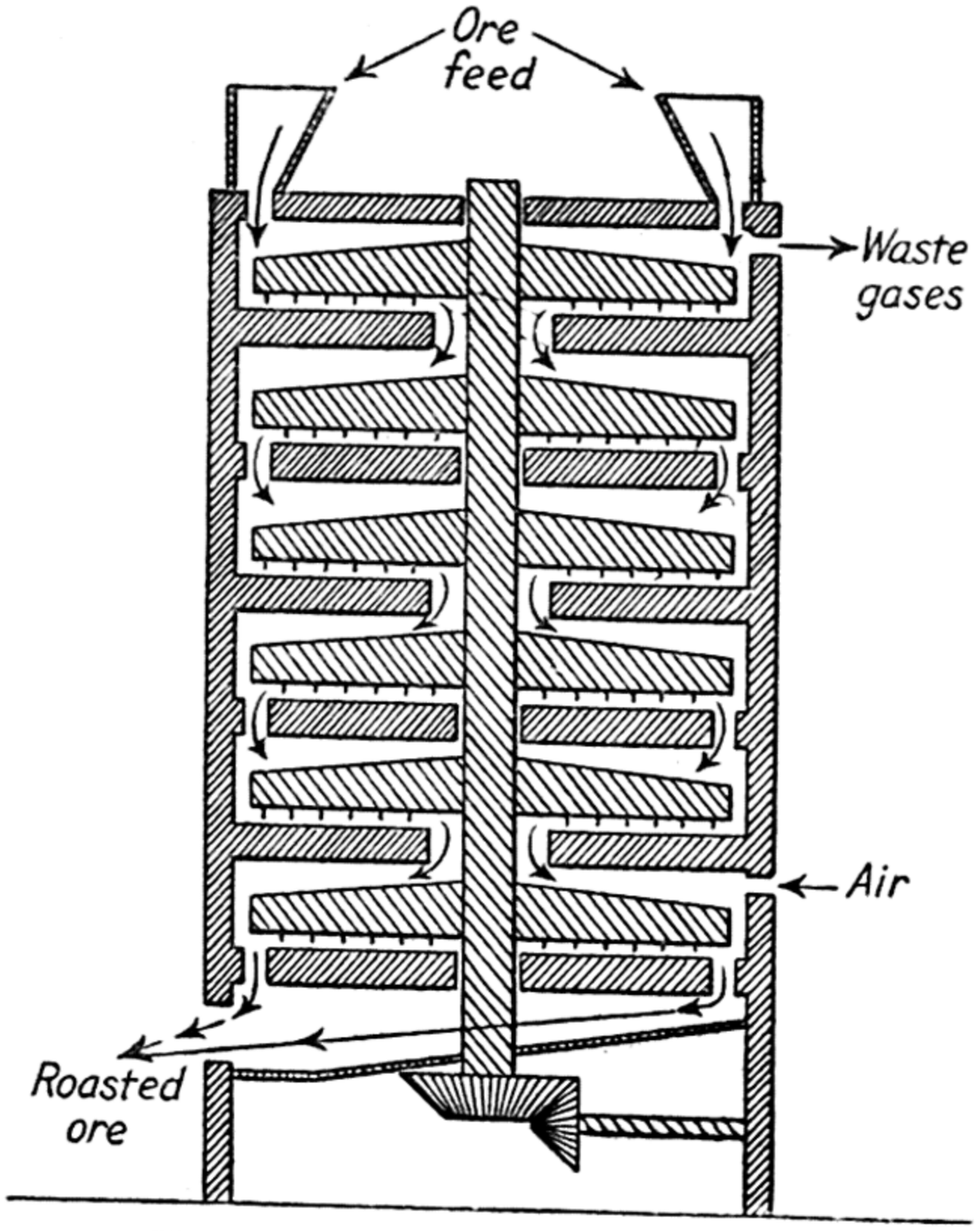


FIG. 161. MacDougal Furnace

with the silica of the sand to form a readily-fusible slag of iron silicate, thus—

$$FeO + SiO_2 = FeSiO_3$$

A mixture composed chiefly of copper sulphide with a little iron sulphide remains behind after the slag has been tapped off. This mixture of sulphides is known as a *matte*, this particular matte being termed *coarse metal.*

The coarse metal is then re-smelted to remove still more of the iron and a *fine metal* is obtained containing about 75 per cent copper and very little iron as sulphide.

Bessemerizing. The molten fine metal is then run into a Bessemer converter lined with basic refractory such as magnesite. Air is blown through the molten charge so oxidizing the sulphur, traces of iron and

other metals, should they be present; the volatile oxides pass out of the converter as gases, whilst the iron oxide forms a slag. Plate II shows a Bessemer converter used for the blowing of copper matte. The reactions involved in Bessemerizing are—

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S = 6Cu + SO_2$$

The molten copper is run into metal moulds. As it cools and finally freezes, the dissolved gases, particularly sulphur dioxide, are evolved since they have lower solubilities in solid copper than they do in the molten metal. Some of the gas bubbles however are entrapped at the moment of

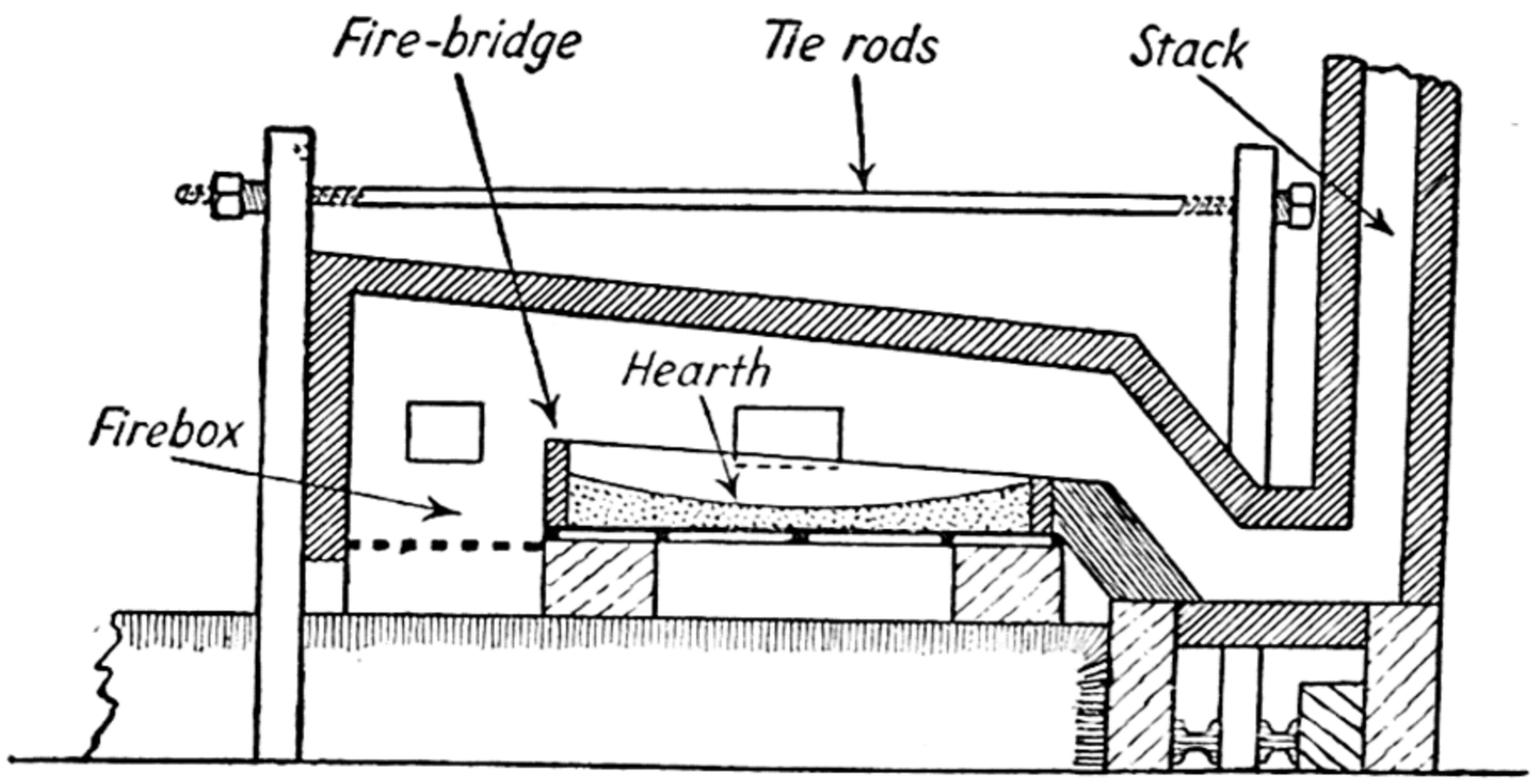


FIG. 162. Reverberatory Furnace

solidification and these give rise to a blistered appearance on the surface of the copper ingots. Hence the term *blister copper* for this material.

Refining of the Blister Copper. Two methods of refining are applied to blister copper; they are (*a*) fire refining, and (*b*) electrolytic refining.

Fire refining involves the re-melting of the blister copper under oxidizing conditions. Thus the various impurities present tend to be removed, the sulphur, lead, zinc, arsenic and antimony as their volatile oxides, whilst manganese, iron, cobalt, nickel and bismuth are removed in the slag. This oxidizing fusion results in the formation of cuprous oxide, Cu_2O, the content of which often rises to about 6 per cent. When this obtains the molten metal is *poled*, that is, stirred with wood poles, the reducing gases evolved causing a reduction of the cuprous oxide (*see* Plate III). The process of poling is continued until the cuprous oxide is almost entirely reduced. When this state of affairs exists a small sample taken with a ladle solidifies in the form of an ingot with a flat top and gives a fracture of flesh-colour with a silky lustre. Copper in this state is known as *tough-pitch* or *tough-cake* copper.

When copper of a higher purity than that obtained by fire-refining is

required, it is necessary to submit the tough-pitch copper to electrolytic refining. In this process, slabs of copper, 3 ft square and about 1 in. thick serve as anodes in an electrolyte consisting of a solution of copper sulphate and sulphuric acid. The cathodes are thin pure copper sheets (*see* Plate III). During the process of electrolysis the base metal impurities tend to pass into solution whilst the precious metals (e.g. gold, silver and platinum) form a deposit on the bottom of the vat, known as *anode slimes*.

The electrolytic copper obtained in this manner is too brittle for use owing to dissolved hydrogen; it is therefore usual to remelt, oxidize the hydrogen, pole again and finally cast into suitable moulds. Such material commonly has a copper content of 99·98 per cent.

Copper from Oxide Ores

Oxidized ores are smelted in blast furnaces with a large percentage of coke. The product is known as *black copper* and its composition depends upon the impurities in the ore. The reaction involved is as follows—

$$Cu_2O + CO = 2Cu + CO_2$$

from the carbon of the coke

Hydrometallurgical Methods

Heap Leaching. This method is used at Rio Tinto in Spain. Sulphide ores are treated by this process in large heaps 10 to 40 ft high. Atmospheric oxygen oxidizes the copper sulphide to copper sulphate. The top of the ore piles is provided with distributing trenches, and solution, at first fresh water, but later waste solution, is directed over the heaps. The passage of the solution through the heap causes the copper sulphate to dissolve and be carried away. About 60 per cent extraction is generally made in the first three years, whilst from seven to nine years are required to bring this up to 80–85 per cent. The copper contained in the solution which runs away from the heaps is precipitated by the addition of iron scrap, thus—

$$CuSO_4 + Fe = FeSO_4 + Cu \downarrow$$

The precipitated copper is then collected, melted, and cast into ingots. It is submitted to refining processes similar to those previously described.

Confined Leaching. This process, as typified by that conducted upon *brochantite* at Chuquicamata in Chile, consists in the loading of the crushed material into vats in which it is soaked in sulphuric acid. A dilute solution of copper sulphate is thus produced. This solution is then electrolyzed in suitable cells in the manner described above.

Physical Properties of Copper

(*a*) Copper is a metal exhibiting a flesh-pink colour.
(*b*) It is very malleable and ductile.

(*c*) It exhibits a high electrical and thermal conductivity; when used for electrical conductors the content of impurities, particularly bismuth, must be maintained below very low limits.

(*d*) Copper readily alloys with many other metals.

Chemical Properties of Copper

(*a*) In dry air, copper is fairly stable at room temperature; if heated, however, it forms cuprous and cupric oxides, the former adjacent to the metal.

(*b*) In moist air a green coating or *patina* is slowly formed on the surface of the metal. The composition of this patina varies according to the composition of the surrounding atmosphere; for example, in inland regions the patina is composed of basic copper sulphate, $CuSO_4 . 3Cu(OH)_2$, whilst under marine conditions it is made up of basic copper chloride, $CuCl_2 . 3Cu(OH)_2$.

(*c*) Dilute sulphuric acid and dilute hydrochloric acid are without action on metallic copper. But in the presence of air these dilute acids act on the metal, thus—

$$2Cu + 4H^+ + \underset{\text{from the air}}{O_2} = 2H_2O + 2Cu^{++}$$

Cold dilute nitric acid acts upon copper as follows—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$

(*d*) Hot concentrated sulphuric acid acts upon copper thus—

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2\uparrow + 2H_2O$$

Heated concentrated nitric acid acts as follows—

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

Hot concentrated hydrochloric acid reacts thus—

$$2Cu + 8HCl = 2H_3CuCl_4 + H_2\uparrow$$

(*e*) Aqueous solutions of caustic alkalis are without action upon copper although fused alkalis attack the metal, forming cupric oxide.

In the presence of the air, aqueous solutions of ammonia react with copper to form a deep-blue coloured solution containing the complex ion $[Cu . 4NH_3]^{++}$.

(*f*) Copper is readily displaced from solutions of its salts by metals which are more electro-positive. Thus—

$$Zn + CuSO_4 = ZnSO_4 + Cu\downarrow$$
$$Fe + CuSO_4 = FeSO_4 + Cu\downarrow$$

Uses of Copper. Copper finds extensive application in industry for the purpose of making electrical conductors, for which the purity must be of

TABLE 81

Typical Compositions of Some of the More Important Copper-base Alloys

Name of Alloy	Typical Composition (percentage by weight)									
	Cu	Zn	Sn	Ni	Al	Pb	P	Cd	As	
Commercial coppers										
Cadmium copper	99·0							1·0		
Arsenical copper	99·5								0·5	
Oxygen-free high-conductivity	99·98									
Brasses										
Red brass	85·0	15·0								
Cartridge brass	70·0	30·0								
Muntz metal	60·0	40·0								
Brazing solder	50·0	50·0								
High-tensile brass	59·7	32·7			3·3					Fe, 2·3 Al, 2·0
Nickel silver										
(*a*)	56·0	24·0		20·0						
(*b*)	45·0	45·0		10·0						
Tin bronzes										
Coinage bronze	95·0		5·0							
Gunmetal	88·0	2·0	10·0							
Bell metal	75·0		25·0							
Speculum metal	68·0		32·0							
Phosphor bronzes										
(*a*)	92·0		7·8				0·2			
(*b*)	84·0		10·0			5·0	1·0			-
Aluminium bronzes										
(*a*)	96·0				4·0					
(*b*)	90·0				10·0					
Copper-nickel alloys										
Constantan	60·0			40·0						
Monel metal	70·0			30·0						

a high order. It is also employed for the manufacture of chemical plant, for steam pipes, for anodes for the electrodeposition of copper and certain of its alloys, and for the manufacture of many compounds of copper.

Probably the greatest tonnage of the metal, however, is expended in the making of alloys. Some of the more important copper-base alloys and their compositions are quoted in Table 81. These alloys provide examples, as indeed do all industrial alloys, of solid solutions. The widespread occurrence, and therefore the importance, of solid solutions will consequently be appreciated.

Cadmium copper finds application for electrical conductors and for such purposes as electrodes for resistance welding machines; it has a higher strength than copper although its electrical conductivity is only slightly less than that of the pure metal. Arsenical copper retains its strength very well at elevated temperatures and therefore finds application for such purposes as locomotive firebox stays, etc. Oxygen-free, high-conductivity copper is employed, as its name implies, for the manufacture of conductors.

The brasses are probably the most important of all the non-ferrous alloys. Red brass and cartridge brass are capable of being fashioned to shape by cold-working processes such as rolling, drawing, stamping, etc., whilst muntz metal is essentially a brass used either for the manufacture of castings (in which the alloy in the molten state is poured into moulds), or for the fabrication of sections by extrusion (i.e. the forcing of the heated, but solid alloy by pressure through a die). Brazing solder is employed for the hard-brazing of ferrous metals. High-tensile brass is sometimes known as *manganese bronze*; these alloys exhibit a high strength, for example a typical value being 42 tons/in.^{2}.

In the case of the nickel silvers, alloy (*a*) is sometimes known as *German silver*; it is outstanding for its good resistance to corrosion, and its ability to take a good polish; alloy (*b*) is employed chiefly in the form of sections for architectural and ornamental purposes.

Of the tin bronzes, gunmetal is employed in the manufacture of high-pressure steam and water fittings; the names coinage bronze and bell metal are self explanatory; speculum metal is a very hard alloy capable of taking a high polish, and is used for the making of mirrors for certain types of optical instruments and for the manufacture of diffraction gratings.

The phosphor bronzes as typified by alloy (*a*) are employed in the cold-worked, and therefore hard, condition for the manufacture of instrument springs and for turbine blading; the alloys as typified by (*b*) are employed in the cast condition for the making of bearings and gears.

Aluminium bronzes of the type quoted under alloy (*a*) are used in the cold-worked state for such purposes as steam turbine condenser tubes;

alloys of the type (*b*) are employed in the cast condition for the manufacture of bearings, gears and forming dies.

Of the copper-nickel alloys, Constantan (also known as *Eureka* and *Ferry*) is used for the manufacture of electrical resistances in which the temperature coefficient must be a minimum; monel metal is widely used as an engineering material on account of the excellent combination of mechanical, physical and chemical properties which it exhibits.

Compounds of Copper

Copper forms two series of compounds, the univalent cuprous compounds, and the bivalent cupric compounds.

The electronic structures of copper, the cuprous ion and the cupric ion are as follows—

	Shell			
	K	L	M	N
Copper . . .	2	8	18	1
Cuprous ion . .	2	8	18	
Cupric ion . .	2	8	17	

All cuprous compounds are white with the exception of the oxide which is red, and the sulphide which is black. The cuprous halides, cuprous oxide, sulphide, cyanide and sulphite are all insoluble in water; cuprous sulphate and acetate are decomposed by water yielding the corresponding cupric salt and copper, thus—

$$Cu_2SO_4 \rightarrow CuSO_4 + Cu$$

Cupric compounds are generally blue or green in colour, an exception being the oxide which is black; generally they are also soluble in water. In their simple compounds both univalent and bivalent copper tend to form covalent rather than electrovalent links.

In dry air cuprous salts are stable, but in the presence of moisture they are slowly oxidized to form basic compounds, thus as shown in equation form above, cuprous sulphate is readily converted by water into the cupric salt and copper. This ease of conversion rather tends to suggest that cupric salts are more stable than are cuprous salts, but this is not necessarily true; for example, cupric iodide, cyanide and thiocyanate decompose spontaneously into the corresponding cuprous compounds, whilst on heating, cupric oxide, sulphide and the halides also suffer conversion in the same way. The instability of these and similar cupric salts is explained by the fact that in cupric compounds the M shell is incomplete, having only

17 instead of 18 electrons as shown above, and the transfer of a single electron from an anion to the cation makes this shell complete. This transfer occurs most readily in those cupric compounds which contain weak electronegative radicals (e.g. iodide, cyanide and thiocyanate). When the electron transfer has been effected the free radicals or atoms unite in pairs to form covalent molecules, thus—

$$Cu^{++} + (CN)' = Cu^{+} + (CN)$$

$$2(CN) = (CN)_2$$

Changes such as that just described occur all the more easily when the cuprous salt is only slightly soluble in water. Thus, soluble cuprous salts decompose in aqueous solution to form cupric salts and copper, whilst cupric salts (whose corresponding cuprous salts are insoluble in water) decompose in aqueous solution to give the cuprous salt which is precipitated. These interactions may be explained by means of the following ionic equation—

$$2Cu^{+} \rightarrow Cu^{++} + Cu$$

Therefore, a soluble cuprous salt which in solution gives rise to a high concentration of cuprous ions, causes the equilibrium to move to the right; whilst, when a cupric salt of an acid, whose cuprous salt is insoluble, is dissolved in water, cuprous ions are removed by precipitation and the equilibrium is moved to the left.

Cuprous Compounds

Cuprous Oxide, Cu_2O. Cuprous oxide is prepared by the action of glucose on Fehling's solution. Fehling's solution is made by adding sodium hydroxide to a mixed solution of cupric sulphate and sodium potassium tartrate. Resulting from the reducing action of the glucose, cuprous oxide is precipitated as a red precipitate which is separated by filtration, washed with hot water and alcohol and finally dried in a vacuum desiccator.

Properties of Cuprous Oxide

(*a*) Cuprous oxide is a red powder.

(*b*) When heated to temperatures below 1000°C, it is converted to cupric oxide CuO, but at temperatures in excess of 1000°C, cuprous oxide is the stable oxide.

(*c*) Cuprous oxide is insoluble in water.

(*d*) It is readily reduced to the metal by heating in an atmosphere of hydrogen or coal gas.

(*e*) With acids, cuprous oxide reacts to form cuprous salts, but these are only stable if they form complex ions with the anion of the acid. In

general, therefore, the action of acids results in the formation of the cupric salt and the deposition of copper. The following reactions are typical—

(i) $$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O$$

(ii) $$Cu_2O + 2HNO_3 = Cu(NO_3)_2 + Cu + H_2O$$

In this case the copper initially formed reacts with further nitric acid to liberate nitric oxide and form more cupric nitrate.

(iii) $$Cu_2O + 2HCl = 2CuCl + H_2O$$

The cuprous chloride dissolves in excess of the acid to form chloro-cuprous acid, thus—

$$2CuCl + 2HCl = H_2Cu_2Cl_4$$

Uses of Cuprous Oxide. Cuprous oxide is used extensively in the glass industry for the manufacture of ruby glass; the colour is probably due to a suspension of colloidal copper in the glass.

Other uses include its application in the manufacture of metal rectifiers and as an ingredient of certain anti-rust paints.

Cuprous Chloride, CuCl. Cuprous chloride is prepared by heating a mixture of cupric oxide and metallic copper with concentrated hydrochloric acid—

$$CuO + Cu + 2HCl = 2CuCl + H_2O$$

The solution is then poured into water when a white precipitate of cuprous chloride is obtained. This precipitate is filtered off, washed with water containing a little sulphur dioxide and then dried either by washing with alcohol and finally ether, or alternatively in a vacuum desiccator.

Cuprous chloride may alternatively be prepared by passing sulphur dioxide through a solution containing equimolecular proportions of cupric sulphate and sodium chloride. The reaction involved is—

$$2CuSO_4 + 2NaCl + 2H_2O + SO_2 = 2CuCl + 2NaHSO_4 + H_2SO_4$$

The cuprous chloride is filtered off and treated as in the previous preparation.

Properties of Cuprous Chloride

(*a*) When pure, cuprous chloride is a white solid, but specimens often contain basic cupric chloride, $3CuO \cdot CuCl_2 \cdot 3H_2O$, due to the action of the moist atmosphere and so exhibit a light green colour.

(*b*) The solid salt is probably an aggregate of cuprous and chloride ions the copper and chlorine being linked covalently in the crystal. Evidence of this method of linkage is provided by the fact that the vapour density of the vapour at 1700°C is only slightly less than that derived from the

formula Cu_2Cl_2. This formula is, therefore, often used for cuprous chloride.

(*c*) Cuprous chloride is practically insoluble in water, but it dissolves in those reagents which enable the copper to form complex ions. Thus in concentrated hydrochloric acid it forms the complex acid, $HCuCl_2$, and in ammonia the ammine, $CuCl \cdot NH_3$. Solutions of both these complexes readily absorb carbon monoxide and hence find application in gas analysis. Carbon monoxide reacts with these solutions to form the carbonyl compound, $CuCl \cdot CO \cdot 2H_2O$, which separates out in the form of colourless crystals. In addition to absorbing carbon monoxide, the ammoniacal solution is also capable of absorbing acetylene which reacts to form a red precipitate of cuprous acetylide, $Cu_2C_2 \cdot H_2O$. This reaction is often employed as a test for the presence of acetylene. Cuprous acetylide is explosive when dry.

Cuprous Iodide, CuI, is precipitated as a white powder mixed with iodine when potassium iodide is added to the solution of a cupric salt, thus—

(*a*) $$2CuSO_4 + 4KI = 2CuI\downarrow + I_2\downarrow + 2K_2SO_4$$

If a reducing agent such as sulphur dioxide is present in addition the precipitate consists entirely of cuprous iodide, thus—

(*b*) $$2CuSO_4 + 2KI + SO_2 + 2H_2O = 2CuI\downarrow + 2KHSO_4 + H_2SO_4$$

Reaction (*a*) is employed in analytical chemistry as a means of determining the concentration of copper in copper-containing solutions. The iodine liberated, equivalent to the amount of copper reacting, is determined volumetrically by titration of the solution with sodium thiosulphate solution.

Cuprous Cyanide, CuCN, is precipitated in an analogous way when potassium cyanide solution is added to cupric sulphate solution.

$$2CuSO_4 + 4KCN = 2CuCN\downarrow + C_2N_2\uparrow + 2K_2SO_4$$

In excess of potassium cyanide solution, cuprous cyanide reacts to form stable potassium cuprocyanide, thus—

$$CuCN + KCN = K[Cu(CN)_2]$$

On dissociation, potassium cuprocyanide gives the following two ions—

$$K[Cu(CN)_2] \rightleftharpoons K^+ + [Cu(CN)_2]'$$

The cuprocyanide ion is very stable indeed, only a small proportion dissociating to give cuprous ions according to the following equation—

$$[Cu(CN)_2]' \rightleftharpoons Cu^+ + 2(CN)'$$

Thus in qualitative analysis when hydrogen sulphide is passed through a mixed solution containing copper and cadmium, to which potassium

cyanide solution has been added in excess, the concentration of cuprous ions is insufficient to precipitate copper sulphide, since the solubility product of this compound is not attained (*see* p. 332). On the other hand, the reaction of potassium cyanide solution with the cadmium results in the formation of the complex salt potassium cadmicyanide, $K_2[Cd(CN)_4]$; the cadmicyanide ion is much less stable than the corresponding cuprocyanide ion. The net result is that the concentration of cadmium ions is sufficiently high to permit the formation of a precipitate of cadmium sulphide since the solubility product of this particular compound is exceeded under the conditions which obtain.

Cuprous Thiocyanate, CuCNS, is a white insoluble compound prepared by adding a soluble thiocyanate, such as potassium thiocyanate, to a solution of cupric sulphate. Initially the precipitate is composed of a mixture of cupric and cuprous thiocyanates, but the cupric salt is rapidly converted to the cuprous salt.

Cupric Compounds

Cupric Oxide, CuO (Black Copper Oxide). On a commercial scale cupric oxide is made by heating malachite, $CuCO_3 . Cu(OH)_2$.

In the laboratory it may be prepared by heating the hydroxide, the carbonate or the nitrate, or by heating the metal in air or in oxygen at temperatures below 1000°C; this last-named method is not very satisfactory unless the copper is in a very finely divided state.

Properties of Cupric Oxide

(*a*) Cupric oxide is a black powder.

(*b*) It is unaffected by heating to approximately 1000°C, but above this temperature it dissociates into cuprous oxide and oxygen, thus—

$$4CuO \rightleftharpoons 2Cu_2O + O_2$$

(*c*) When heated with reducing agents such as carbon monoxide, hydrogen and carbon it is readily reduced to the metal.

(*d*) It is insoluble in water.

(*e*) Cupric oxide is a typical basic oxide reacting with acids to form the corresponding cupric salts.

Uses of Cupric Oxide. Apart from its use in the laboratory as an oxidizing agent in chemical analysis, cupric oxide finds application in industry in the manufacture of coloured glasses and ceramics, to which it imparts either a green or a blue colour, probably due to the formation of copper silicate.

Cupric Hydroxide, $Cu(OH)_2$. This compound is formed as a pale-blue precipitate of a gelatinous nature when a solution of either sodium or potassium hydroxide is added to a cold solution of a cupric salt, thus—

$$CuSO_4 + 2NaOH = Cu(OH)_2 \downarrow + Na_2SO_4$$

If the solution is heated, a black precipitate results of the compound $3CuO \cdot Cu(OH)_2$. This basic compound may be regarded as the genesis of such basic salts as basic cupric chloride, $3CuO \cdot CuCl_2 \cdot 3H_2O$.

Properties of Cupric Hydroxide

(*a*) When heated, cupric hydroxide loses water and forms cupric oxide.

(*b*) Cupric hydroxide is insoluble in water and also in sodium and potassium hydroxide solutions.

(*c*) It reacts with ammonium hydroxide initially to form a precipitate of cupric hydroxide but this dissolves in excess of ammonium hydroxide to give a deep-blue coloured solution known as *Schweitzer's reagent*, a solution of cupri-tetrammine hydroxide, $[Cu \cdot 4NH_3](OH)_2$. This solution possesses the power of dissolving cellulose, the cellulose being reprecipitated when the "solution" is acidified. This fact is of considerable technical importance since it is the basis for the manufacture of one type of rayon, or artificial silk. In this process the "solution" of cellulose is squirted through extremely fine orifices or "spinerets" into a solution of dilute acid when the cellulose is precipitated into the form of long threads; these threads are drawn upon reels, washed, dyed, and fabricated into garments.

(*d*) Cupric hydroxide reacts readily with acids forming the corresponding cupric salts.

Cupric Carbonate is unknown as the normal salt. Thus, the addition of a solution of sodium carbonate to a solution of a soluble cupric salt such as cupric sulphate results in the formation of a green coloured precipitate composed of a mixture of basic cupric sulphate and basic cupric carbonate.

Basic cupric carbonate occurs in nature in the form of such minerals as *malachite*, $CuCO_3 \cdot Cu(OH)_2$, and *azurite*, $2CuCO_3 \cdot Cu(OH)_2$.

Cupric Chloride, $CuCl_2$. Anhydrous cupric chloride is formed when chlorine in excess is passed over copper maintained at a temperature not in excess of approximately 250°C. If higher temperatures are employed the cupric chloride dissociates into cuprous chloride and chlorine. The anhydrous salt may also be prepared by passing hydrogen chloride over the hydrated salt maintained at or below the temperature quoted above.

The dihydrate may be prepared by the action of hydrochloric acid on either cupric oxide or the basic carbonate; on evaporation of the solution crystals of the dihydrate $CuCl_2 \cdot 2H_2O$ separate out.

Properties of Cupric Chloride

(*a*) Anhydrous cupric chloride is a brown powder.

(*b*) The salt dissolves in water, concentrated solutions being brown in colour, but on dilution they turn green and finally become blue. These colour changes are due to the preponderance in concentrated solutions

of the complex anion $[CuCl_4]''$, whilst dilution with water gives rise to the formation of a larger proportion of the complex cation $[Cu.4H_2O]^{++}$.

Addition of concentrated hydrochloric acid or a concentrated solution of potassium chloride to the blue solution turns it brown in colour again; the common ion effect is thereby demonstrated.

(*c*) Cupric chloride is a very deliquescent substance.

Uses of Cupric Chloride. In industry, cupric chloride finds application in the pigment known as *Brunswick Green;* this pigment is made by boiling cupric sulphate solution with bleaching powder when a mixture of the basic chloride and cupric sulphate (Brunswick Green) is obtained.

Cupric Sulphate (Blue Stone or Blue Vitriol), $CuSO_4$. Cupric sulphate is the most important salt of copper and is used in industry on a very large scale.

On a commercial scale cupric sulphate is made by spraying hot dilute sulphuric acid on to copper scrap or turnings contained within a lead-lined tower up which a current of air is blown. The reaction involved is as follows—

$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O$$

from the air blown up the tower

It is also manufactured by the regulated roasting of copper pyrites, $CuFeS_2$ in a current of air. The copper is converted into cupric sulphate, whilst the iron is oxidized to ferric oxide. The cupric sulphate is then leached out of the roasted mass by extraction with water.

In both these processes the resulting solution of cupric sulphate is evaporated when crystals of the pentahydrate $CuSO_4 . 5H_2O$ separate out. Cupric sulphate is also obtained as a by-product of the Mond nickel process.

Properties of Cupric Sulphate

(*a*) The anhydrous salt is colourless, but the hydrated salt is blue in colour.

(*b*) Cupric sulphate is readily soluble in water although it is insoluble in ethyl alcohol.

(*c*) If the pentahydrate is heated it loses four molecules of water of crystallization at 100°C, and if heated to 250°C the anhydrous salt is formed.

$$CuSO_4 . 5H_2O \xrightarrow[100°C]{} CuSO_4 . H_2O \xrightarrow[250°C]{} CuSO_4$$

The anhydrous salt is often used as a means of detecting the presence of moisture which, if present, turns the colourless anhydrous salt to the blue-coloured pentahydrate.

If the anhydrous salt is heated still further it forms a basic sulphate and at

still higher temperatures (e.g. 700°C) the oxide is formed with the liberation of sulphur trioxide.

(*d*) Cupric sulphate absorbs hydrogen chloride as follows—

$$CuSO_4 + 4HCl = H_2[CuCl_4] + H_2SO_4$$

This reaction is employed in gas analysis for the absorption of hydrogen chloride from gaseous mixtures.

Uses of Cupric Sulphate. Cupric sulphate is employed in large quantities for the electroplating of copper and copper-base alloys such as brasses and tin bronzes. It is also the raw material from which many copper compounds are made. It also finds application in calico printing and in the manufacture of certain dyestuffs. Cupric sulphate acts as a fungicide and its solution with slaked lime is employed, under the name of *Bordeaux mixture*, for the spraying of grape-vines, potatoes, etc. It is also used as a preservative for timber.

Cupric Nitrate, $Cu(NO_3)_2$, is made by the action of nitric acid upon either metallic copper, or basic copper carbonate. On evaporation of the resulting solution deep blue crystals of the trihydrate $Cu(NO_3)_2 . 3H_2O$ separate out. The anhydrous salt is white.

When the trihydrate is heated, it first loses water of crystallization and nitric acid to form the basic nitrate, $Cu(NO_3)_2 . 3Cu(OH)_2$ which at higher temperatures is decomposed yielding cupric oxide, nitrogen peroxide, oxygen and water.

Copper Acetates. The normal acetate, $Cu(CH_3COO)_2 . H_2O$, is made by the action of acetic acid on either cupric oxide or upon *verdigris*. This compound finds application in the manufacture of green pigments.

Basic cupric acetate, or verdigris, is produced when metallic copper is exposed alternately to the air and to the residues left after the fermentation of grapes. Two varieties of this material are distinguished; they are *blue verdigris*, $Cu_2O(CH_3COO)_2$, and *green verdigris*, $CuO . Cu(CH_3COO)_2$.

SILVER

Occurrence. Silver occurs in nature both in the form of the metal and also in chemical combination with other elements. Native silver is mined in Mexico, in Nevada, at Broken Hill in New South Wales, and in Bolivia. Silver forms a natural alloy with gold; for example, the gold mined in the Rand in Transvaal, South Africa, contains about 10 per cent silver. Silver is also obtained as a valuable by-product in the electrolytic refining of copper (*see* p. 457).

The chief source of the world's silver, however, is the silver sulphide mineral *argentite*, Ag_2S (also known as *silver glance*) which is present to some extent in almost all deposits of galena, the chief ore of lead, and often in appreciable amounts. *Horn silver* or *cerargyrite*, AgCl, which occurs also in lead deposits, also contributes to the world's supply of silver.

Thus, more than half of the world's silver is obtained not from silver mines but from argentiferous lead, zinc and copper ores as a by-product. It has been estimated that the silver-bearing ores which yield 91 per cent of the world's silver also yield 85 per cent of the world's supply of gold, 69 per cent of the lead, 66 per cent of the copper, and 46 per cent of the zinc. Argentiferous lead-zinc ores are mined at Broken Hill, New South Wales, the famous mines of Cerro de Pasco in Peru, the Potosi mines in Bolivia, Mexico and Nevada.

Extraction of Silver

Silver is extracted by means of the following processes—

(1) The Cyanide process (also known as the MacArthur-Forrest process).

(2) The Parkes's process for the desilverization of lead.

(3) The Luce-Rozan process.

(4) Electrolytic methods applied to—

(*a*) the refining of lead (Betts process); and

(*b*) the refining of copper.

The Cyanide Process. In this process the ore, crushed to a fine state of division, is digested in large vats in a solution of sodium cyanide. The silver and/or the silver compounds react as indicated by the following equations—

(*a*) $$4Ag + 8NaCN + 2H_2O + \underset{\text{oxygen from the air}}{O_2} = 4Na[Ag(CN)_2] + 4NaOH$$

Silver sulphide and silver chloride dissolve without oxygen, thus—

(*b*) $$AgCl + 2NaCN = Na[Ag(CN)_2] + NaCl$$

(*c*) $$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

this last reaction being reversible and requiring excess cyanide to ensure completion. The strength of the sodium cyanide solution is from 0·2–1·0 per cent. After a time the solution tends to become exhausted owing to the accumulation of salts such as sodium sulphide, etc. The silver-bearing solution is then run off from the vats and allowed to flow over boxes made of wood, steel or cement, containing zinc shavings, when the following reaction occurs—

$$Zn + 2Na[Ag(CN)_2] = 2Ag\downarrow + 2NaCN + Zn(CN)_2$$

The silver is collected, melted down, and purified electrolytically.

Parkes's Process. This process depends upon the facts that molten lead and molten zinc are immiscible, and that silver is more soluble in molten zinc than in molten lead.

The silver-bearing lead is melted down in furnaces of about 25 tons capacity and about 1 per cent of zinc added; the temperature of the furnace is allowed to fall and the zinc-silver alloy which separates out is skimmed from the furnace continuously. It should be noted that the molten zinc

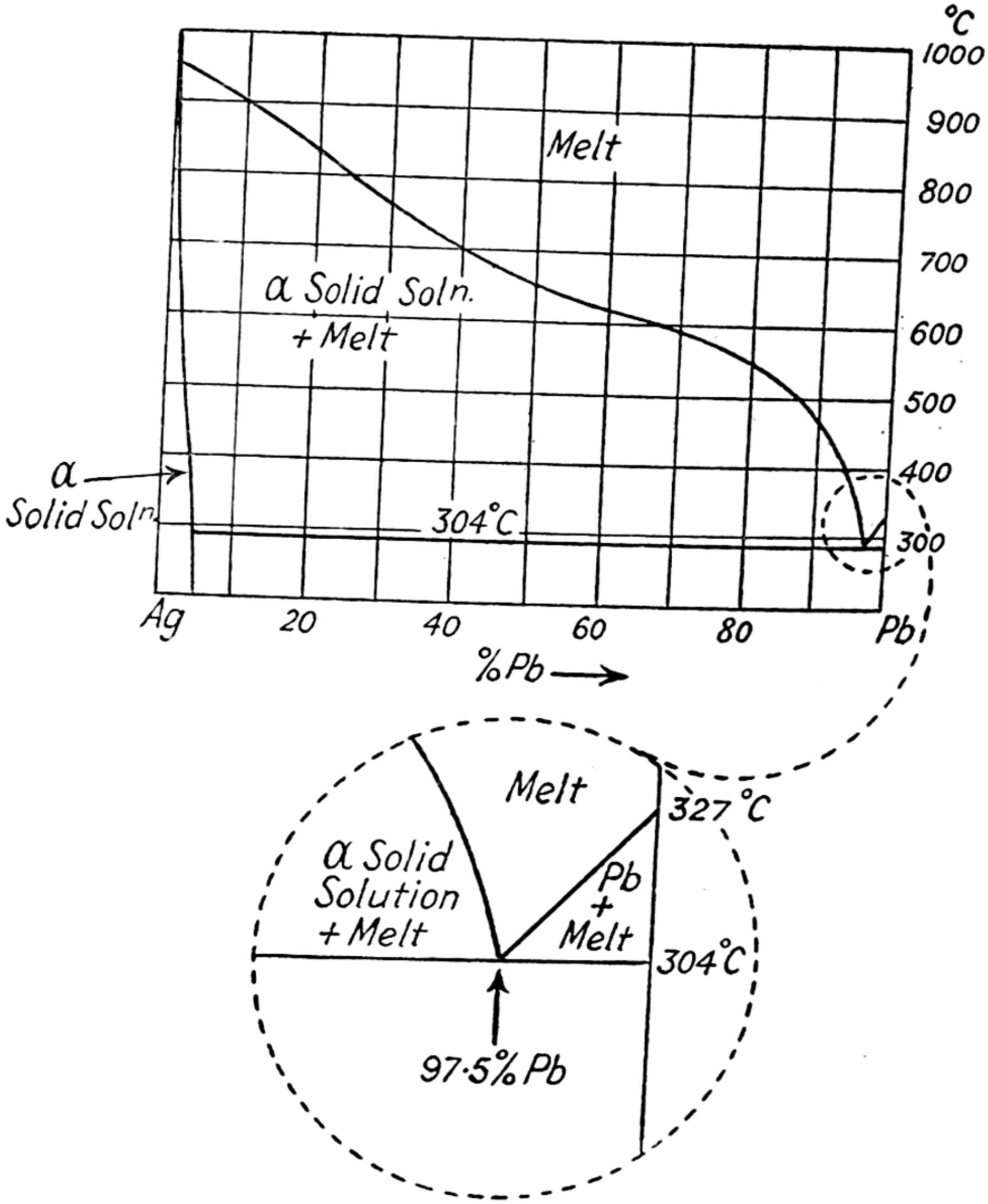


FIG. 163. Equilibrium Diagram for Silver–Lead System

floats on top of the molten lead. These skimmings, contaminated with lead, are transferred to a retort and distilled with charcoal to reduce any oxide present. The zinc is recovered as distillate, a lead-silver alloy remaining in the retort. The silver is then obtained from this residue by cupellation (*see* p. 471).

Luce-Rozan Process. This process is a modification of the older Pattinson's process, the latter only being employed to a small extent at the

present time. The Luce-Rozan process depends upon the fact that when molten low-grade, silver-bearing lead is cooled to its freezing point, crystals of lead separate out which are very much poorer in silver than the still liquid original lead. This will be clear from a consideration of the thermal equilibrium diagram of the silver-lead system as shown in Fig. 163. From this diagram it will be noted that the eutectic composition between these two metals occurs at 2·5 per cent silver. The crystals of high purity lead which separate on cooling are removed by means of a perforated ladle. Since the crystals which separate cannot be freed completely from adhering (and hence silver-containing) liquid alloy it is usual to repeat the melting and cooling process with the skimmings obtained from this first pot. Fresh lead of similar precious metal content is added to the first pot and the melting and cooling procedure repeated. In this way there is obtained for the market a refined lead low in precious metal content whilst the balance is left in the form of a lead—enriched in silver—ready for cupellation. This enriched lead contains about 2 per cent silver. Two melting pots are used in this process, each holding about 7 tons of lead; the crystallizing pot holds about 20 tons of lead. In the crystallizer the lead is agitated by means of steam blast; cooling is effected by withdrawal of the fire and by water sprays.

Electrolytic Methods (*a*) *Betts Process.* In this method, argentiferous lead is electrolytically refined using fluosilicic acid, H_2SiF_6, lead fluosilicate, $PbSiF_6$, and gelatine or glue, as electrolyte. The silver-bearing lead is cast into anodes, the cathodes being made from thin sheets of refined lead. The silver, along with other precious metals, is recovered from the electrolyte as anode slimes which are then worked up by furnace methods for the precious metal content.

(*b*) *Electrolytic copper refining.* In a similar manner, anode slimes produced during the electrolytic refining of copper (*see* p. 457) are worked up for their precious metal contents.

Cupellation. The lead-containing precious metals obtained from the Parkes's process or the Luce-Rozan process are treated by cupellation for the recovery of the precious metals. This process consists essentially of melting the rich lead in a reverberatory furnace and exposing it to a blast of air, whereby the lead and other base metals are oxidized and slagged off in the form of litharge of varying degrees of purity, whilst the precious metals, silver, gold and the platinum metals, having no affinity for oxygen under these conditions remain behind in the metallic state. The oxidation is effected mainly by the air blast and partially by means of the molten litharge which absorbs an excess of oxygen and passes it to the underlying impurities (e.g. copper, arsenic, tellurium and selenium). The separation of the precious metals from one another is effected by means of the processes of *parting*.

Parting of Silver and Gold Bullion. Various methods are employed for

the separation or parting of silver, gold and the platinum metals from one another. Two methods will be described here, both electrolytic processes; they are—

(*a*) The Balbach process.
(*b*) The Wohlwill process.

The Balbach Process. In this process ingots of the bullion are made the anodes in cells made of earthenware capable of holding about 20 gallons of electrolyte. The electrolyte consists of an aqueous solution of 0·5 per cent nitric acid along with about 5 per cent silver and 5 per cent copper. The anodes rest on trays lined with canvas cloth to retain the slimes formed during electrolysis. The cathode consists of graphite sheets forming the bottom of the tank. The current employed is about 200 amperes at 5 volts. On electrolysis the silver dissolves from the anodes and is deposited in the form of fine crystals on the graphite cathode, these crystals are removed, washed, dried, and melted down. The purity of these silver ingots is 99·97 per cent or more of silver. The other precious metals are left as black anode slimes.

The Wohlwill Process. The black anode slimes from the Balbach process are melted down and cast into anodes for use in the Wohlwill process. The electrolyte is a 5 per cent aqueous solution of hydrochloric acid containing 5–8 per cent of gold as chloride. The electrolyte is maintained at about 60°C, and is agitated by blowing in air. The cathodes are thin sheets of fine gold. The current supply used is a direct current on which is superimposed an alternating current of slightly higher voltage, the latter causing the silver chloride formed on the surface of the anode to fall off and thus not interfere with further solution of the anode. Gold is deposited on the gold cathodes; platinum also dissolves from the anode with the gold, but is not deposited on the cathodes; it is precipitated in the solution, from time to time, by the addition of ammonium chloride.

Physical Properties of Silver

(*a*) Silver is a lustrous white metal capable of taking a high polish.
(*b*) It is very malleable and ductile but less so than gold.
(*c*) Its electrical and thermal conductivities are higher than those of any other substance.
(*d*) It is a comparatively soft metal.
(*e*) Its density is 10·5.
(*f*) It has a high melting point (960°C)

Chemical Properties of Silver

(*a*) At ordinary temperatures silver is not attacked by oxygen, but at its melting point molten silver will absorb more than 20 times its own volume of oxygen without losing its lustrous appearance. On solidification

this dissolved oxygen is almost completely thrown out of solution, the oxygen evolution being sufficiently violent to cause minor eruptions on the surface of the melt. This phenomenon is known as *spitting*, and is possibly due to the occurrence of supercooling caused by the presence of the dissolved oxygen.

(*b*) Exposure of silver at ordinary temperatures to industrial atmospheres results in the formation of a thin black film of silver sulphide, Ag_2S, by interaction with the gaseous sulphurous compounds present in such atmospheres. This staining may be prevented by alloying the silver with small contents of beryllium. The sulphide film is sometimes produced artificially, when it is termed "oxidized silver," by treatment of the surface of the metal with an aqueous solution of a soluble sulphide such as sodium sulphide. When such films are lightly polished on certain portions of the surface an attractive finish is produced.

The blackening of silver egg spoons is also due to the formation of silver sulphide, the sulphur in this case being derived from the egg.

(*c*) Silver combines directly with the halogens, particularly at elevated temperatures.

(*d*) Silver is not acted upon by dilute sulphuric acid, but in the hot concentrated acid it dissolves readily, thus—

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 \uparrow + 2H_2O$$

Dilute hydrochloric acid is also without action on the metal, and even hot concentrated hydrochloric acid only has a slight action on silver forming silver chloride; at red heat, hydrogen chloride reacts with silver to form silver chloride.

Nitric acid, no matter whether dilute or concentrated, cold or hot, dissolves silver, forming silver nitrate and liberating oxides of nitrogen.

(*e*) Silver is not attacked by ammonia nor by caustic alkalis, whether the latter be in the fused state or in aqueous solution.

Uses of Silver. The commercially pure form of silver is known as "fine silver" to distinguish it from "standard" or "sterling silver," which contains 7·5 per cent copper; this latter alloy is that which is hall-marked in Great Britain, the British Empire, and the United States of America. Sterling silver was the legal standard of British coinage from the time of Queen Elizabeth until 1920 when the price of silver was so high that the alloy had become more valuable as a metal than as a token, the silver content was therefore reduced to 50 per cent, the remainder being made up of 40 per cent copper, 5 per cent nickel, and 5 per cent zinc. This composition was maintained until recently when, after the Second World War, conditions compelled the decision to replace the present British "silver" currency by one of 75:25 cupro-nickel.

Silver is used in large quantities for the manufacture of certain items of chemical plant, for which it has been used in parts of some 4 cwt in weight.

The qualities which make silver so attractive for such purposes are freedom from oxidation, resistance to various chemical acids and caustic alkalis, high thermal and electrical conductivities and a good combination of mechanical properties. Silver has replaced copper in many cases. Very large tonnages of silver are employed for the manufacture of silver nitrate. This compound is chiefly used in the photographic industry.

Silver is used for anodes for the electrodeposition of silver; only high quality electrolytic silver is suitable for this purpose, the metal normally having a content of 99·98 per cent silver. Silver electrodeposits are used for conductors in the radio and electrical engineering industries and for the lining of certain types of bearings used in high-duty engines.

Standard silver is widely employed in the jewellery trade, such goods usually being submitted to one or other of the assay offices for hall marking.

Large quantities of silver are used in the manufacture of silver solders. Three types are commonly recognized containing 60, 50 and 40 per cent silver respectively; the alloying elements are copper, zinc and cadmium.

The Compounds of Silver

The atom of silver is able to form two series of compounds, (*a*) argentous and (*b*) argentic. The electronic structures of silver, the argentous ion and the argentic ion are as follows—

	Shell				
	K	L	M	N	O
Silver . .	2	8	18	18	1
Argentous ion .	2	8	18	18	
Argentic ion . .	2	8	18	17	

A silver atom is capable of forming a single electrovalent bond by the transfer of its single O electron (*see* above) to an electronegative element or radical, or of forming a single covalent bond by sharing its O electron as one member of a shared electron pair. Such compounds are termed argentous compounds and it is probable that the more simple ones, e.g. AgCl, are electrovalent rather than covalent in character.

The argentous ion is also capable of forming both anionic as well as cationic complexes with such molecules as ammonia. Simple argentous compounds are white in colour. Exceptions to this statement are the oxide, which is brown, and the iodide which is yellow.

In the presence of water simple argentous salts do not decompose (cf. cuprous salts).

Of the argentic compounds the only one which need be mentioned here is the fluoride, Ag_2F, which is a strong oxidizing agent.

Silver Oxide, Ag_2O (Argentous Oxide), is made by adding sodium hydroxide solution to a solution of silver nitrate. It is a dark-brown coloured substance, it is only very slightly soluble in water, but the moist oxide exhibits an alkaline reaction. It is thus a basic oxide and reacts with acids to give the corresponding silver salts, thus—

$$Ag_2O + H_2SO_4 = Ag_2SO_4 + H_2O$$

It reacts with ammonium hydroxide to form silver ammine hydroxide, $[Ag . 2NH_3]OH$, which on standing deposits *fulminating silver*, Ag_3N. When heated the oxide dissociates according to the following reaction—

$$2Ag_2O \rightleftharpoons 4Ag + O_2$$

Silver Chloride, AgCl (Argentous Chloride), occurs naturally as Horn Silver. It may be prepared in the laboratory by adding the solution of a soluble chloride to a solution of silver nitrate. The silver chloride is precipitated in a fine state of division which is capable of coagulation by boiling. This precipitate is insoluble in dilute acids but dissolves in ammonium hydroxide solution with the formation of the complex cation, $[Ag . 2NH_3]^+$. The solid chloride absorbs ammonia gas with the formation of such ammines as $AgCl . 2NH_3$ and $AgCl . 3NH_3$. Silver chloride also dissolves in aqueous solutions of sodium thiosulphate and potassium cyanide with the formation of the complexes, $[Ag . (S_2O_3)_2]'''$ and $[Ag . (CN)_2]'$, respectively.

TABLE 82

The More Important Physical Properties of the Silver Halides

Property	Fluoride	Chloride	Bromide	Iodide
Colour	White	White	Pale yellow	Light yellow
Solubility in water (mg/litre of water at 25°C) . .	180g/100g of water	1·6 mg	0·133 mg	0·0023 mg
Melting point (°C) . .	435	455	422	556
Crystal structure . .	—	Rock salt	Rock salt	Three possible forms of existence
Weight dissolved in 100 g 10 per cent ammonium hydroxide solution at 12°C	—	7·84 g	0·35 g	0·0036 g

Silver chloride exhibits only a very slight solubility in water and this fact constitutes the basis of a test to detect the presence either of silver or of chlorides.

Silver chloride, like the other silver halides, darkens on exposure to light, a property which is utilized in photography.

The chemistry of the other silver halides is very similar to that of the chloride as described above. *Silver fluoride*, AgF, is made by the action of hydrofluoric acid on argentous oxide; this halide differs from the other three silver halides in that it is readily soluble in water. *Silver bromide*, AgBr, and *silver iodide*, AgI, may be prepared by precipitation methods analagous to that employed for the preparation of silver chloride. The table on p. 475 gives details of some of the more important physical properties of the silver halides.

Photographic Chemistry

The first action of light when it falls upon a silver halide is to cause transference of an electron from the halogen ion to the silver ion, thus—

$$Ag^+ + Cl' \rightleftharpoons Ag + Cl$$

(e transferred from Cl' to Ag^+)

The reversibility of the reaction should be noted since if the halogen is prevented from escaping it recombines with the silver when the light is shut off. In the ordinary way the halogen escapes and a permanent deposit of silver is formed. The same effect is produced more rapidly if the halide is mixed with some substance which will combine with the halogen as it is formed; gelatine is such a substance and this material is therefore used in the manufacture of photographic emulsions, the gelatine serving both as a vehicle for the halide, and also as an electron acceptor. Silver citrate is also used for this same purpose.

Thus when a photographic emulsion is exposed to light in a camera a small amount of silver halide is reduced to metallic silver, but the image is invisible to the naked eye since the exposure is so short. However, if the photographic emulsion is immersed in a solution of a suitable reducing agent known as a *developer* (such as hydroquinone) then the chemical reduction of the silver halide continues wherever the light has fallen upon the emulsion. Thus, there is produced a "negative" in which dark areas represent those regions where the light originally fell upon the emulsion and light areas where the emulsion did not receive any incident light. In the negative the light and dark areas are the reverse of those which obtained in the original image.

In order to render the developed emulsion permanent to light it is customary to *fix* the developed emulsion by immersion in a solution of sodium thiosulphate (hypo) when the silver halide dissolves to form complex salts as previously described. This fixing of the emulsion is

quite necessary since otherwise the areas remaining light after development would darken progressively on subsequent exposure to light. This process of development must, of course, be conducted in a "dark room," a room illuminated solely by light of such a colour (either deep red or dark green according to the type of emulsion used) that the emulsion will not be "fogged" during processing.

Positive prints are obtained from the washed and dried negative by exposing to light through the negative a paper coated with an emulsion also composed of gelatine and silver halides. If the halide is silver chloride the printing paper may be printed in daylight, the resulting print being rendered permanent by immersion in hypo solution after which it is washed with water and dried. If the emulsion coating the paper contains silver bromide, the printing paper—often termed "gaslight" or "contact" paper—may be printed by very short exposure (5–30 seconds) to a source of artificial light such as an electric light bulb; after printing in this way the print is developed and fixed in a similar manner to that described above for negatives.

With the object of rendering a photographic emulsion more sensitive to red light it is usual to incorporate certain dyestuffs in the emulsion; such photographic materials are said to have *panchromatic* emulsions. These are the materials which must be processed in light of a dark-green colour, or in complete darkness.

Silver Nitrate, $AgNO_3$ (Lunar Caustic). This is probably the most important of all the compounds of silver.

Silver nitrate is made by the action of nitric acid upon the metal. When the solution is evaporated the salt crystallizes in the form of large transparent, anhydrous plates. Silver nitrate is sometimes melted and cast into sticks.

Properties of Silver Nitrate

(*a*) Silver nitrate is very soluble in water; for example, 100 g of water at 0°C dissolve 122 g of the salt, and at 100°C, 952 g.

(*b*) The aqueous solution of silver nitrate is not hydrolyzed.

(*c*) No hydrates are formed by this salt.

(*d*) Silver nitrate is an oxidizing agent and even at atmospheric temperature is reduced to metallic silver by organic substances. For example, a solution of silver nitrate is often used as a marking ink for linen; on contact with the textile the metallic silver is precipitated within the fibre where it cannot be easily removed by washing.

(*e*) On heating it melts at 217°C, and at approximately 450°C, it decomposes to yield *silver nitrite*, $AgNO_2$; at still higher temperatures, 650–700°C, the nitrite decomposes to yield metallic silver and liberate oxides of nitrogen and oxygen, thus—

$$2AgNO_3 = 2Ag + 2NO_2 \uparrow + O_2 \uparrow$$

(*f*) Silver nitrate in the solid state absorbs ammonia gas to form the compound $[Ag . 3NH_3]NO_3$, whilst from an aqueous solution of silver nitrate to which ammonium hydroxide has been added, crystals of $[Ag . 2NH_3]NO_3$ may be obtained by evaporation. This solution, often known as *ammoniacal silver nitrate* is used in organic chemistry as a reagent for detection of reducing agents. Such ammoniacal solutions may be regarded as containing dissolved argentous oxide and on reaction with a reducing agent the oxide is reduced to metallic silver. If this test is conducted in a test tube the metal is deposited in the form of a brilliant silver mirror on the walls of the test tube. Thus, acetaldehyde, a typical organic reducing agent, reacts as follows—

$$\text{“}Ag_2O\text{”} + \underset{\text{Acetaldehyde}}{CH_3CHO} = 2Ag\downarrow + CH_3COOH$$

This reaction is facilitated by gentle warming.

(*g*) Silver nitrate exhibits a cauterizing action on human skin; hence the name *lunar caustic*.

Uses of Silver Nitrate. The most important use for silver nitrate is in connexion with the photographic industry in which the salt is converted into the halides of silver.

It is also used in the laboratory as a reagent and also in chemical analysis for the volumetric determination of chlorides, bromides, cyanides and thiocyanates; it is also employed to detect a reducing agent as described above.

Other applications include its use in surgery as a cauterizing medium; and also as a marking ink on linen, etc.

Silver Cyanide, AgCN, is formed as a white precipitate when potassium cyanide solution is added to the solution of a soluble salt, such as silver nitrate, thus—

$$AgNO_3 + KCN = AgCN\downarrow + KNO_3$$

Silver cyanide is soluble in excess of potassium cyanide solution, giving a colourless solution of potassium argentocyanide—

$$AgCN + KCN = K[Ag(CN)_2]$$

Potassium argentocyanide solution is the chief constituent of silver plating baths. Dissociation of the electrolyte occurs as follows—

(*a*) $$K[Ag(CN)_2] \rightleftharpoons K^+ + [Ag(CN)_2]'$$

(*b*) $$[Ag(CN)_2]' \rightleftharpoons Ag^+ + 2(CN)'$$

There are, therefore, four different ions in solution, K^+, Ag^+, and the $(CN)'$ ions.

In electroplating practice the anodes are of fine silver and the articles

to be plated constitute the cathode. During electrolysis, silver is deposited on the cathode, the loss of silver ions from the electrolyte being made good by the dissolution of silver from the anode by the action of the cyanide ions. In this way the strength of the plating bath is maintained.

GOLD

Occurrence. Gold occurs very widely distributed in nature, chiefly in the free state, when it is invariably alloyed to a greater or less extent with silver or copper, and occasionally with bismuth, mercury, and other metals.

Most of the world's gold is obtained from what is known as *native gold.* This native gold has been known to contain as much as 99·8 per cent gold, but as a rule it varies from 85–95 per cent, the remainder usually being mainly silver. When the silver content is high the naturally occurring alloy is known as *electrum.* After native gold in importance are the tellurides, the chief of which is *calaverite*, $(AuAg)Te_2$ with 43 per cent gold. Gold is also recovered as a by-product from certain base-metal ores such as those of copper, lead and zinc.

Extraction of Gold

Gold ores may be classified into two groups—

(1) Free-milling ores, from which the native gold is recoverable by crushing and amalgamation; and

(2) Refractory ores, that is, tellurides and auriferous sulphides, which yield their gold by a complex smelting process.

Gold often occurs unaltered and concentrated, because of its insolubility and high density, in alluvial or in placer deposits. The gold in such deposits is derived from the weathering and disintegration of gold-bearing lodes or veins. The gold in placers varies in size from mere "colours" to that of nuggets, some of which have weighed over 200 lb.

Placer deposits are not always found on the surface; for example the famous Rand gold deposits of the Transvaal, South Africa, are old or fossil placers.

Auriferous quartz veins constitute the commonest and most productive kinds of gold deposits. Examples of such deposits are the famous Kolar goldfield in India, mines in Brazil and in the Gold Coast.

Native gold may be recovered from alluvial deposits by water concentration processes, followed by amalgamation with mercury. "Free milling ores" occurring in veins are milled and ground prior to amalgamation. When the ore is partially "refractory," or when the gold is very finely divided, cyanidation is employed. Often treatment by amalgamation is followed by cyanidation of the tailings for the recovery of the unamalgamated very fine gold and combined gold.

Before the fine grinding of ores and treatment with cyanide, it is sometimes necessary to roast the ores in order to remove arsenic and antimony as their volatile compounds, since these elements if present lead to decomposition of the cyanide with the accompanying excessive consumption of this material.

Water Concentration Processes. These processes depend upon the fact that the density of gold is much greater than that of associated minerals, etc. Thus, when sand and gravel containing particles of gold are agitated with water the particles of gold tend to form a layer on the bottom of the vessels whilst the sand, etc., tends to be carried off with the agitating water. This principle is employed in placer mining in which the gravel is agitated in sluices fitted with transverse riffles along the bottom. A powerful stream of water flows through the sluice and carries the gravel along with it, but the gold tends to sink and is caught by the riffles.

Amalgamation. A pulp of the "fines" is caused to flow over slightly inclined copper plates amalgamated with mercury; the gold amalgamates with the mercury and is retained on the plates whilst the pulp flows on. The amalgamation process is also employed in connexion with the pulp obtained by crushing gold-bearing quartz in stamp batteries. The amalgam is scraped periodically from the plates and heated in large retorts when the mercury is removed by distillation leaving an alloy of gold and silver. The mercury is recovered and used again. This impure material is then refined as described under the refining of silver.

MacArthur-Forrest Process or Cyanide Process. In principle this process is the same as that described for the extraction of silver (*see* p. 469). In the case of gold extraction the reactions involved are—

(*a*) $4Au + 8NaCN + O_2 + 2H_2O = 4Na[Au(CN)_2] + 4NaOH$

(*b*) $Zn + 2Na[Au(CN)_2] = Na_2[Zn(CN)_4] + 2Au \downarrow$

The gold is then purified, as described in the case of silver on p. 471.

Physical Properties of Gold

(*a*) Gold exhibits a yellow lustrous colour.

(*b*) It is the most ductile of metals; for example a single ounce of gold can be drawn into a wire 50 miles long.

(*c*) It is also the most malleable of metals. It may be rolled and finally beaten into sheets or leaves of only one to two hundred-thousandths of an inch in thickness. Very thin gold sheets are translucent and transmit a green light.

(*d*) Gold is a very heavy metal, density 19·3.

(*e*) It has a high melting point, i.e. 1063°C.

(*f*) After silver and copper, gold is the next best conductor of heat and electricity.

Chemical Properties of Gold

(*a*) Gold is unaffected by the atmosphere or oxygen at any temperature, or by water, or by sulphur.

(*b*) It is hardly affected by hydrochloric, sulphuric and nitric acids, but it is attacked by "aqua regia," a mixture of nitric acid and hydrochloric acid in the proportion of 1:3, since this mixture readily evolves chlorine on warming, the gold dissolving to form aurichloric, or chlorauric acid, $H[AuCl_4]$, thus—

$$Au + 4HCl + HNO_3 = H[AuCl_4] + NO + 2H_2O$$

Gold is also attacked by hot selenic acid, by aqueous solutions of either sodium or potassium cyanides when exposed to the oxygen of the air, and by fused alkalis and nitrates.

(*c*) Gold is attacked rapidly by chlorine and bromine at atmospheric temperatures.

Colloidal Gold. Colloidal solutions of gold are readily made by reducing the solutions of gold salts with such reducing agents as formaldehyde, Rochelle salt (sodium potassium tartrate), etc.

The pigment known as *Purple of Cassius* is a colloidal solution of gold and stannic hydroxide prepared by adding a mixture of stannous and stannic chlorides drop by drop to an aqueous solution of a gold salt. This is an example of the *protection* of a colloid, the colloidal stannic acid protecting the gold particles. A red suspension of gold is obtained when formaldehyde is added to a dilute solution of a gold salt. A blue colloidal solution is obtained when hydrazine hydrate is used as the reducing agent.

Uses of Gold. The principal use of gold is as the standard for monetary systems in the form of ingots, that is, as "bullion."

Its next most important use is for the fabrication of jewellery for which purpose gold is hardened by alloying it with copper, silver, palladium, or nickel. The purity or "fineness" of gold is expressed in parts per 1000, or as a number of *carats*. Thus pure gold is 24 carat, but usually the highest value for jewellery is 22 carats, although lower carat values, i.e. 9, 12, 15 and 18 are also employed.

Gold is also used in the form of electrodeposited coatings on articles which must be submitted to use in corrosive media. Gold salts are also used in the photographic industry and "Purple of Cassius" finds application in the manufacture of ruby glass. Gold leaf is used for the external gilding of ornaments on public buildings and monuments.

Compounds of Gold

Gold forms two series of compounds, the monovalent aurous compounds, and the trivalent auric compounds. The auric compounds are covalent and probably the simple aurous are covalent also.

When gold is dissolved in aqua regia, *aurichloric acid* is formed,

$H[AuCl_4] . 4H_2O$ which may be separated in the form of yellow crystals on evaporation. If these crystals are heated to approximately 120°C, *auric chloride*, $AuCl_3$ is produced. When heated to 175°C, this compound decomposes yielding *aurous chloride*, AuCl and evolving chlorine. Auric chloride is soluble in water, in alcohol, and in ether.

Aurichloric acid forms its corresponding sodium and potassium salts, $Na[AuCl_4] . 2H_2O$ and $K[AuCl_4] . 2H_2O$. Other examples of anionic complexes formed by auric gold include potassium auricyanide, $K[Au(CN)_4]$, potassium aurate, $K[AuO_2] . 3H_2O$, and potassium auribromide, $K[AuBr_4]$.

The aurichlorides find application in the photographic industry whilst the auricyanides constitute the chief constituents of gold electroplating baths.

CHAPTER 20

THE ELEMENTS OF GROUP II

THE elements of Group II fall into two sub-groups; (*a*) the alkaline earth metals, and (*b*) zinc, cadmium and mercury. The elements beryllium, magnesium, calcium, strontium and barium constitute what are known as the "Alkaline Earth Metals." These metals are strongly electropositive, this property increasing, as in the case of the alkali metals, as the atomic weight increases.

THE ALKALINE EARTH METALS

All these metals are grey in colour, are of moderate hardness, and have high melting points. Like the alkali metals, they are all capable of reacting with water but less vigorously. In aqueous solution their salts do not suffer hydrolysis to any great extent.

In all their compounds the alkaline earth metals exist as bi-electrovalent cations. The normal electrode potentials of these metals constitute a measure of the ease with which they form cations; their readiness to form cations is also shown by the stability of the metallic oxides towards reducing agents, and by the basic nature of their hydroxides.

The chemistry of magnesium, calcium and barium is very similar in many ways to that of sodium and potassium. Thus, the ions of the three first-named are colourless, their hydroxides are basic and their sulphides are soluble in water. On the other hand the compounds of the alkaline earth metals are more readily decomposed by heating than are the corresponding compounds of the alkali metals, and in addition their hydroxides are weaker, and their salts are more readily hydrolyzed. Many of the salts of the alkaline earth metals are insoluble in water, whereas those of the alkali metals are outstanding for their general solubility.

Beryllium, the lightest element of this group shows many resemblances to aluminium, mercury and to zinc. Beryllium and magnesium also show a number of close resemblances to one another, although the latter also shows some resemblance to lithium. Some of the more important physical characteristics of the alkaline earth metals are given in Table 83 on p. 484.

BERYLLIUM

Occurrence. The only important source of beryllium is the mineral known as *beryl*, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$ which contains about 5 per cent of the metal. This mineral is of fairly widespread occurrence, the chief

TABLE 83

Some Physical Characteristics of the Alkaline Earth Metals

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba
Atomic number	4	12	20	38	56
Electronic configuration	2, 2	2, 8, 2	2, 8, 8, 2	2, 8, 18, 8, 2	2, 8, 18, 18, 8, 2
Atomic weight	9·02	24·32	40·08	87·63	137·36
Density (g/cm³ at 20°C)	1·85	1·74	1·55	2·6	3·5
Atomic volume (cm³/g atom)	4·96	14·0	25·86	33·7	39·25
Melting point (°C)	1285·0	650·0	851·1	772·2	850·0
Boiling point (°C) (760 mm pressure)	2780·0	1107·0	1487·2	1384·0	1638·0
Thermal conductivity (cal/cm²/sec at 20°C)	0·3847	0·37	—	—	—
Electrical resistivity (microhm-cm)	18·5	4·46	4·6	22·76	—
Normal electrode potential (Hydrogen scale) (volts)	— 0·81	— 1·55	— 1·9	— 2·07	— 2·15

deposits being found in Argentina, Brazil, Canada, India, Portugal and South Africa.

The mineral *gadolinite*, $2BeO \cdot FeO \cdot 2Y_2O_3 \cdot 2SiO_2$, is often referred to as a commercial source of beryllium, though its occurrence is comparatively rare. This mineral is, however, more of importance as a source of the element yttrium rather than beryllium.

Extraction of Beryllium. Various methods have been employed for the extraction of beryllium from the mineral beryl. Many difficulties, however, are experienced if attempts are made to extract the metal by the orthodox methods. One of the great obstacles to recovering beryllium is its extreme lightness (density = 1·85), and the slags produced by chemical reduction are often heavier than the metal so that the metal floats on top of the slags instead of being protected by them. Similarly, in electrolytic production, the fused electrolyte is often heavier than the liberated metal, with the result that difficulty is experienced in preventing the beryllium from taking fire at the anode. The lightness of beryllium is one of the chief reasons why it is much easier to produce a *master alloy* of beryllium rather than the pure metal.

A typical modern extraction method is that operated at Degussa (Frankfurt) in which the metal is obtained by the electrolytic reduction of the chloride obtained from beryl after a lengthy, preliminary process involving (*a*) digestion with an alkali metal carbonate followed by (*b*) digestion in hydrochloric acid to remove silica, and (*c*) treatment with an alkali metal hydroxide to remove aluminium. The precipitate of beryllium hydroxide obtained by this last treatment is then converted to the chloride by treatment with hydrochloric acid.

The pure beryllium chloride obtained in the manner described above is mixed with an equal weight of sodium chloride and electrolyzed in a nickel crucible at a temperature of 350°C, using 40–50 volts at 500 amp. The nickel crucible, which is heated externally by means of resistance elements, also serves as the cathode; the anode is a graphite rod which passes through the lid of the crucible. Metallic beryllium is deposited in the form of dendritic flakes along the walls of the nickel crucible. When electrolysis is complete the flakes of beryllium are washed off, pressed into briquettes by hydraulic pressure and pre-melted at 1400°C in a beryllium oxide crucible under an atmosphere of hydrogen. Final melting and casting are conducted in a vacuum of 10^{-3} mm of mercury. After re-melting the metal has a purity of 99·8 per cent, the rest being chiefly oxide.

Physical Properties of Beryllium.

(*a*) Beryllium is a white metal similar in appearance to magnesium and aluminium.

(*b*) Beryllium has the highest melting point of the alkaline earth metals (i.e. 1285°C).

(*c*) In the pure (that is, the distilled) form, the metal is sufficiently malleable to be capable of forging and hot-rolling to some extent, but it becomes brittle again on cooling.

(*d*) With the exception of the alkali metals, beryllium is the lightest of all the metals; its density is 1·85 (about one third lighter than aluminium).

Chemical Properties of Beryllium

(*a*) Beryllium exhibits a great affinity for oxygen; for example in powder form it burns when ignited in air, giving a brilliant light.

(*b*) At atmospheric temperature it is impervious to the action of the air and water; it does not react with water even at red heat. It is thus free from a tendency to tarnish.

(*c*) Beryllium has little affinity for sulphur.

(*d*) It dissolves in acids to form the corresponding beryllium salts.

(*e*) Beryllium dissolves in the aqueous solutions of caustic alkalis.

Uses of Beryllium. The most important application of beryllium arises from its ability to impart heat-treatable characteristics to copper, nickel, cobalt and iron, its alloys with the first of the four named metals being the most important.

The heat-treatment of 2·25 per cent beryllium-copper alloy gives it a strength about six times that of soft copper. Sometimes these beryllium-copper alloys are termed *beryllium bronzes*. This increase in strength is accompanied by a much smaller reduction in electrical conductivity than would attend the use of other hardening agents, such as silicon or tin. By heat-treatment of beryllium coppers a hardness equivalent to about 90 tons/in.^{2} is obtained. Such figures as these compare very favourably with those of tool steel—indeed beryllium copper chisels are sufficiently hard to cut mild steel. The non-pyrophoric nature of beryllium copper renders it spark-proof and therefore very suitable for use in dangerous atmospheres. Beryllium copper is finding increasing application for engineering components which must exhibit a high resistance to wear. These alloys are also employed for the manufacture of instrument springs instead of the more orthodox spring steel.

Beryllium is also used in the form of plates, obtained by pressing the metal at red heat, for the manufacture of "windows" for X-ray tubes. Because of its low atomic weight beryllium permits X-rays to pass through seventeen times better than does aluminium, the metal previously used for this application; it is also used for the manufacture of electrodes for neon signs; as a coating for steel in order to enable this material to resist better the attack of hydrogen at high temperatures, such as those obtaining in the Bergius process of coal hydrogenation; and also for the de-oxidation of copper. In this last named application, beryllium is replacing phosphorus more and more since a cast copper of much higher electrical

conductivity results, with the consequent saving of weight and cost of parts of electrical applicances, etc.

Compounds of Beryllium

The chemistry of the compounds of beryllium is dominated by the fact that beryllium has a very low atomic volume. Beryllium compounds are largely covalent.

Beryllium oxide (beryllia) BeO can be obtained by heating the metal, carbonate, hydroxide or nitrate in air. On a commercial scale it is made from the mineral beryl. Beryllium oxide is a white powder having an extremely high melting point. It dissolves in acids to form the corresponding beryllium salts, and in alkalis to from beryllates (e.g. sodium beryllate, Na_2BeO_2).

The salts of beryllium are similar to those of magnesium in properties but they also resemble the salts of aluminium, for example in respect of the volatility and hydrolysis of the chloride.

Beryllium oxide is used as a refractory for the manufacture of crucibles; beryllium nitrate finds application for strengthening the oxide skeletons of incandescent mantles. When beryl is substituted for felspar in the manufacture of porcelain the resulting product exhibits a very high electrical resistance and low coefficient of thermal expansion so that such porcelains are very suitable for use in connexion with the manufacture of such electrical components as sparking plugs.

MAGNESIUM

Occurrence. Magnesium, which is estimated to constitute 2·7 per cent of the earth's crust, is far too reactive to be found free in nature. Magnesium is the sixth most abundant element in the earth, following oxygen, silicon, aluminium, iron and calcium in the order named. The ores of magnesium used for extraction of the metal and the production of its compounds are extremely widely distributed. The chief magnesium minerals are as shown on p. 488.

Large deposits of *brucite* are worked in Ontario and Quebec in Canada, and in Nevada in the U.S.A. Deposits of *magnesite* are found in Greece, at Satka in the Ural Mountains of the U.S.S.R., at Veitsch in Austria and in the State of Washington, U.S.A. *Dolomite* is found far more abundantly than is magnesite; beds of dolomite and of dolomitic limestone (a mineral containing a higher content of limestone than is indicated by the formula of dolomite) occur in the Dolomite Alps of the Tyrol, and in Britain in the counties of Yorkshire, Derbyshire, Nottinghamshire and Durham. The sulphates and chlorides occur in the well-known Stassfürt salt deposits in Germany.

Besides the naturally occurring minerals tabulated on p. 488, magnesium is also found as a constituent of sea water and of deep well brines,

and in the waters of certain inland seas (e.g. the Dead Sea). Ocean sea water contains about 0·5 per cent magnesium chloride which is equivalent to about 0·14 per cent magnesium, but magnesium-bearing bitterns often have higher magnesium contents than this.

Type of Compound	Name of Mineral and its Formula
Oxide	Periclase, MgO Brucite, $MgO.H_2O$ Spinel, $MgO.Al_2O_3$
Carbonate	Magnesite, $MgCO_3$ Dolomite, $MgCO_3.CaCO_3$
Sulphate	Epsomite, $MgSO_4.7H_2O$ Kieserite, $MgSO_4.H_2O$ Polyhalite, $MgSO_4.K_2SO_4.2CaSO_4.2H_2O$ Kainite, $MgSO_4.KCl.3H_2O$
Chloride	Carnallite, $MgCl_2.KCl.6H_2O$
Silicate	There are many magnesium silicates occurring in nature, most of them are complex in constitution. The more common include talc, $3MgO.4SiO_2.H_2O$, and asbestos, a very complex silicate of magnesium, calcium and other metals.

Extraction of Magnesium

Less than forty years ago magnesium was a metal of only very minor use, but at the present time it is extracted on a tremendous scale. Two methods are employed for the production of metallic magnesium, they are—

(1) Thermal reduction of magnesium oxide (magnesia).
(2) Electrolytic reduction of fused magnesium chloride.

The magnesium chloride may be obtained from natural salt deposits such as those at Stassfürt, or be prepared from oxide or from carbonate ores by chlorination; the magnesia may be obtained from sea water or from carbonate ores. At the present time the magnesium occurring in sea water constitutes an exceedingly important source of the metal, since the supply of magnesium compounds in sea water may be regarded as more or less inexhaustible. A cubic mile of sea water, on the basis of its content of 0·14 per cent magnesium, contains over four million tons of the metal.

Production of Magnesia from Sea Water

The production of magnesia from sea water is based on the almost total insolubility of magnesium hydroxide in water. The successful manufacture of magnesia from sea water depends upon the following factors—

(*a*) The means to soften the sea water cheaply.

(*b*) The preparation of a purified lime slurry of correct characteristics.

(*c*) The economical removal of the precipitated hydroxide from the large volume of water undergoing treatment.

(*d*) The inexpensive purification of the hydrated precipitates.

(*e*) The satisfactory and cheap filtration of the viscous slimes produced.

The sea water is pumped into pre-treatment tanks, in which a little lime is added to react with the dissolved calcium bicarbonate. Calcium carbonate is precipitated and much of it settles in the tanks, that which is in suspension being removed by means of sand filters. Calcined dolomite is then slaked with water and the resulting "milk" produced is sprayed on to the surface of the water contained in large reaction tanks. The water, bearing magnesium hydroxide in suspension, then flows into a settling tank from whence slurry of constant concentration is pumped to screens and then to heating tanks. Here it is heated by steam to facilitate filtering through cotton vacuum filters, on the outside of which the magnesia forms a cake. The cake is extruded in fine threads and is then fed to the rotary kilns. These kilns, like those employed in cement manufacture, are fired by pulverized fuel.

For thermal processes of magnesium production the fully-calcined magnesia is required; for electrolytic methods of production a reactive caustic magnesia is preferred. Instead of calcined dolomite, certain plants use a pure lime obtained by the calcination of oyster shells. In such plants, however, the whole of the magnesium comes from the sea water undergoing treatment, whereas when calcined dolomite is used as calcining material only one half of the magnesium comes from the sea water, the remainder coming from the dolomite. The result is that plants using dolomite are much smaller and the cost of production is lower.

The chemical reactions involved in processes such as those described above are as follows—

(i) *Calcination of dolomite* (or limestone, that is oyster shells, etc.)—

(*a*) $$CaCO_3 . MgCO_3 = CaO + MgO + 2CO_2 \uparrow$$

(*b*) $$CaCO_3 = CaO + CO_2 \uparrow$$

(ii) *Slaking of the calcined dolomite* (or limestone)—

(*a*) $$CaO + H_2O = Ca(OH)_2$$

(*b*) $$CaO + MgO + 2H_2O = Ca(OH)_2 + Mg(OH)_2$$

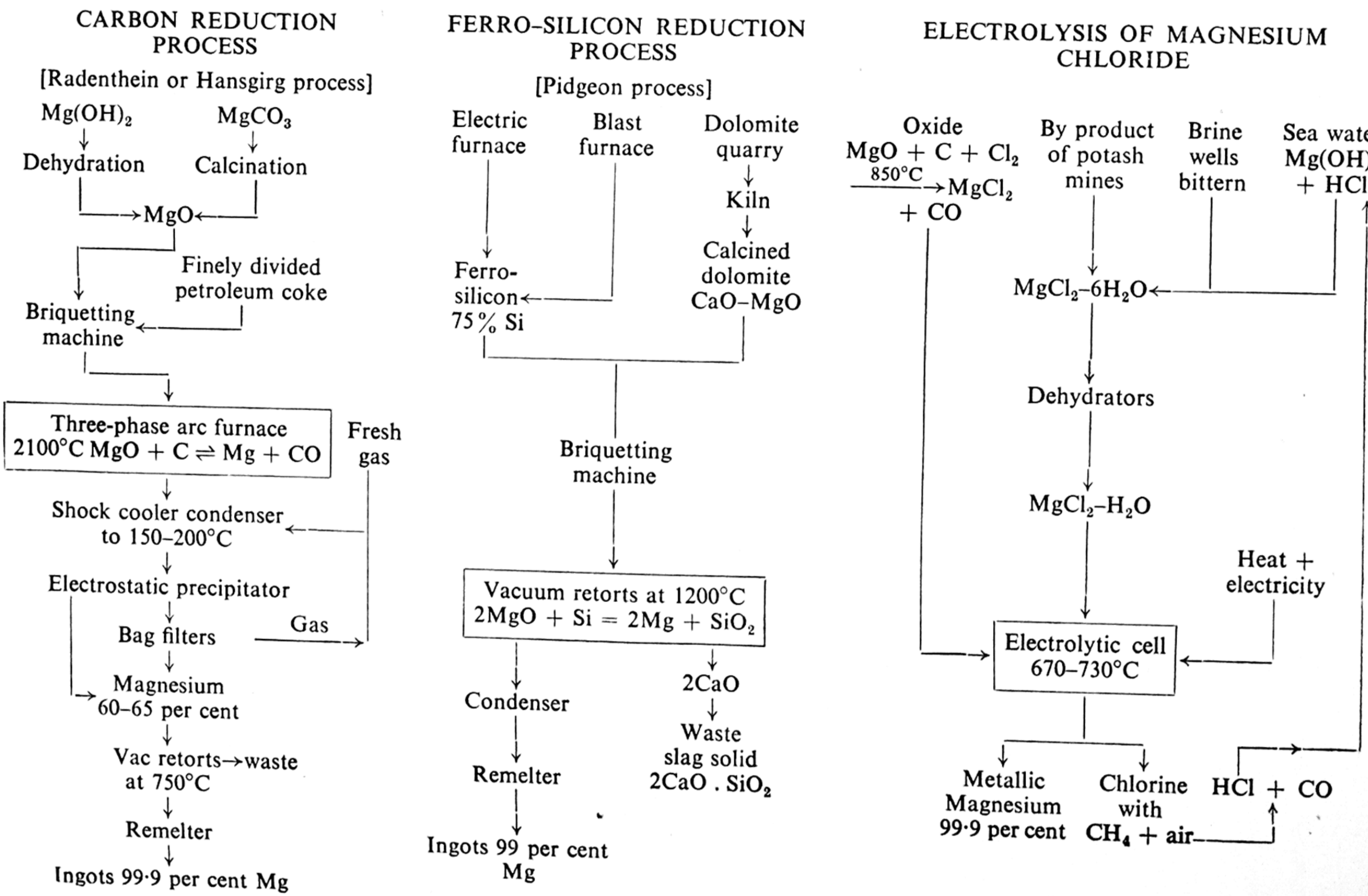


FIG. 164. Outline of Processes for Production of Metallic Magnesium

(iii) *Precipitation treatment of the sea water*—

(*a*) With slaked and calcined dolomite

$$2Ca(OH)_2 + 2Mg(OH)_2 + MgCl_2 + MgSO_4 = 4Mg(OH)_2\downarrow + CaCl_2 + CaSO_4$$

(*b*) With slaked and calcined lime

$$MgCl_2 + MgSO_4 + 2Ca(OH)_2 = 2Mg(OH)_2\downarrow + CaCl_2 + CaSO_4$$

(iv) *Calcination of the precipitated magnesium hydroxide*—

$$Mg(OH)_2 = MgO + H_2O$$

Production of Metallic Magnesium

An outline of the processes for the production of metallic magnesium is given in Fig. 164.

Carbon Reduction Process (Radenthein or Hansgirg Process). The reduction of magnesia by carbon takes place according to the apparently simple equation—

$$MgO + C \rightleftharpoons Mg\uparrow + CO\uparrow$$

It should be noted, however, that this reaction is reversible, carbon monoxide acting as an oxidizing agent when the temperature is 1800°C, or lower. The reduction, must therefore be conducted at a very high temperature, normally a temperature of approximately 2000°C, is used and the difficulty of reversibility at lower temperatures overcome by "shock-cooling" of the magnesium vapour by dilution with an inert gas such as hydrogen. Thus, the magnesium vapour is drawn off from the reduction furnace (an electric arc is used) by suction from a jet of strongly-cooled hydrogen. In this way the temperature of the vapour is quickly brought down to a temperature of about 200°C, and the reverse reaction suppressed to such an extent that the condensed dust contains only about 10 per cent oxide. The condensed dust is compressed and sublimed in retorts at 750°C under a high vacuum. The furnace used for the initial reduction of the magnesia is a totally-enclosed, carbon-brick-lined three-phase electric arc furnace.

Ferrosilicon Reduction Process (Pidgeon Process). In this process the furnace charge is made by mixing ground, dead-burned dolomite with ground ferrosilicon and pelleting. The pellets are then charged into a chromium alloy steel retort equipped with a condenser tube and a removable lining. The retort is heated to a temperature of 1100–1250°C by means of external resistance-heating elements, the reaction being run at a pressure of less than 4 mm of mercury. The chemical reaction involved is as follows—

$$2(MgO\,.\,CaO) + Si = 2CaO\,.\,SiO_2 + 2Mg\uparrow$$

The magnesium vapour condenses to form a mass of crystals inside

the condenser. At the end of the run the furnace is partly cooled and the magnesium removed from the condenser by the differential contraction of the magnesium and the steel. The magnesium does not require any additional purification.

The Pidgeon process has the advantage over the carbon reduction process in that much lower temperatures may be used for the reduction and also that there is not the same possibility of explosion of magnesium dust suspended in air.

The calcium originally present in the calcined dolomite remains in the retort as dicalcium silicate which is reasily removed at the end of the run.

By Electrolytic Reduction. Magnesium is obtained by the electrolytic reduction of fused magnesium chloride. Magnesium chloride may be obtained in various ways—

(i) from salt deposits such as those at Stassfürt,
(ii) from brine wells,
(iii) from the reaction of magnesium hydroxide (from sea water or from dolomite) with hydrochloric acid; and
(iv) from the reaction of magnesia (from sea water or from dolomite) with carbon and chlorine.

Magnesium is extracted by the electrolysis of fused magnesium chloride by Magnesium Elektron Ltd., in Britain, the Dow Chemical Company in the U.S.A., and the I.G. Farbenindustrie in Germany. The chloride is obtained from magnesium hydroxide by treating with hydrochloric acid, and the solution is then evaporated to give $MgCl_2 . 6H_2O$. This salt dehydrates easily to $MgCl_2 . 2H_2O$ and the anhydrous salt is obtained by heating in an atmosphere of hydrogen chloride. In the manufacture of the chloride from magnesia, the oxide is mixed with coal, peat moss and a binder, and chlorinated at about 850°C in an electrically-heated furnace in an atmosphere of chlorine. Molten anhydrous magnesium chloride is produced according to the reaction—

$$MgO + C + Cl_2 \xrightarrow[850°C]{} MgCl_2(l) + CO\uparrow$$

Electrolysis of the magnesium chloride is conducted in firebrick-lined, rectangular steel cells. There are six steel cathodes and three anodes made of graphite bars suspended vertically in the electrolyte, and shielded to collect the chlorine (*see* Fig. 165). Sodium chloride is added to the bath to lower the melting point of the magnesium chloride and also to increase the electrical conductivity. The cells are heated by gas-fired furnaces to keep the bath molten.

On account of its low density, the magnesium floats on the surface and it is therefore necessary to provide for the complete separation of the anode and cathode compartments, in order to prevent contact between the magnesium liberated at the cathode and the chlorine liberated at the anode,

with the consequent chemical reaction. The dividing partitions are of ceramic material suspended from above. The operating temperature of the cells is between 670 and 730°C. (*Note*: Melting point of magnesium is 650°C.) The voltage is 7–9 volts, and the current density 16–35 amp/in.^{2}. The molten magnesium floating on the surface of the electrolyte is protected from oxidation by a thin coating of electrolyte. From time to time molten magnesium is skimmed off and transferred in ladles to the plant for casting into ingots. The purity of the metal produced is higher than 99·9 per cent magnesium.

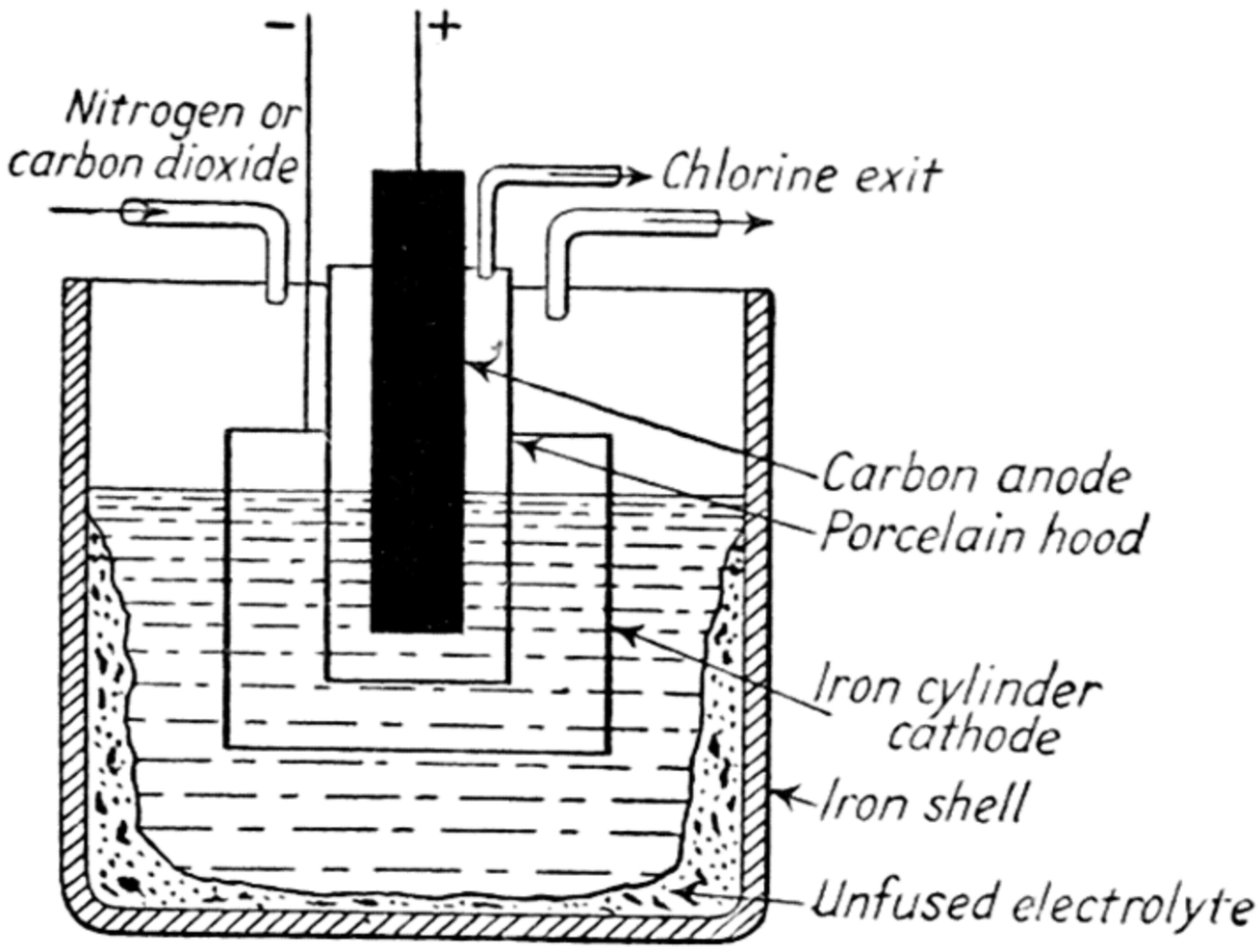


FIG. 165. Electrolytic Production of Magnesium

Physical Properties of Magnesium

(*a*) Magnesium is a silvery-white metal.

(*b*) It has a density of 1·74, and is the lightest metal employed for structural purposes. Magnesium weighs about two-thirds that of an equal volume of aluminium.

(*c*) The metal has a high melting point (650°C) and a high boiling point (1107°C). When heated in vacuo, magnesium sublimes and deposits crystals.

(*d*) Magnesium is about 25 per cent stronger than aluminium and is also harder, but has inferior working properties.

(*e*) The electrical conductivities of equal weights of magnesium and aluminium are about the same.

(*f*) Magnesium exhibits good machinability.

Chemical Properties of Magnesium

(*a*) In dry air (*at room temperature*) magnesium is stable, but in moist air it becomes coated with a film of the oxide in the first instance and then the hydroxide and the carbonate. This film tends to act as a protection

but various chlorides, for example, sodium chloride in salt spray, dissolve it and thus render it ineffective. Ammonium chloride also dissolves this film, hence the use of this compound in qualitative analysis previous to the separation of Group 3 (iron, chromium and aluminium) in order to prevent the precipitation of magnesium along with these elements when ammonium hydroxide solution is added.

(*b*) When the temperature of magnesium is raised to the region of its melting point the metal takes fire and burns with a brilliant white light to form, when in an atmosphere of oxygen, the oxide, (magnesia) MgO. This combustion is facilitated by using the metal in the form of ribbon or powder. Magnesium dust very readily explodes. In air the combustion results in the formation of the oxide and the nitride, Mg_3N_2. Massive magnesium does not burn in this manner in air except at temperatures considerably in excess of the melting point.

(*c*) When magnesium is heated it combines directly with sulphur, chlorine, phosphorus, boron and carbon to form the sulphide, chloride, phosphide, boride and carbide respectively. It does not form a hydride nor a derivative of ammonia corresponding to sodamide.

(*d*) Magnesium, when heated in a current of steam, takes fire, forming the oxide and liberating hydrogen, thus—

$$Mg + H_2O = MgO + H_2 \uparrow$$

Similar reactions occur when the metal is heated in sulphur dioxide and in carbon dioxide, magnesium oxide being formed in each case and elemental sulphur and carbon liberated respectively.

(*e*) When heated, magnesium will also reduce such stable oxides as carbon monoxide, silicon dioxide, and the oxides of sodium and potassium.

(*f*) Dilute acids dissolve the metal rapidly, with the formation of the corresponding magnesium salts and the evolution of hydrogen, thus—

$$Mg + H_2SO_4 = MgSO_4 + H_2 \uparrow$$

The metal also dissolves in aqueous solutions of salts which are acidic because of hydrolysis.

(*g*) Caustic alkalis have no action on magnesium.

(*h*) Magnesium reacts with dry alkyl halides to form organo-magnesium compounds known as "Grignard reagents." The general equation representing the formation of Grignard reagents is as follows—

$$C_nH_{2n+1}X + Mg = C_nH_{2n+1} \cdot MgX$$

where X = Cl, Br or I.

(*i*) Since magnesium is a strongly electropositive element it will displace many metals from solutions of their salts.

Uses of Magnesium. Magnesium is employed in quantities for the manufacture of Grignard's reagents. Magnesium ribbon and wire are

used largely by the radio industry for de-gassing radio valves. It is also used in the foundry industry for the de-oxidation of copper-, brass- and nickel-base alloys.

The greatest tonnage of magnesium, however, is used for the manufacture of alloys. Magnesium-base light alloys are the lightest known useful alloys for engineering construction, the Elektron series being particularly notable. Similar series are the Magnuminium series and the Dow metal series as produced by the Dow Chemical Company in the U.S.A. Many of these alloys are capable of being heat-treated whereby their mechanical properties may be enhanced. Table 84, gives the composition of some typical alloys.

TABLE 84

Typical Magnesium-base Light Alloys

Use of Alloy	Percentage				
	Mg	Al	Zn	Mn	Ni
For the manufacture of castings . .	98·5			1·5	
	88·7	9·0	1·0	0·3	
For the manufacture of forgings, tubes, etc.	85·0	11·0	1·5	1·0	1·5

Magnesium is also used as a minor constituent of many other alloys.

Compounds of Magnesium

Magnesium Oxide, (Magnesia) MgO. Magnesium oxide may be prepared in the laboratory by heating magnesium nitrate, hydroxide, or the basic carbonate. It is also formed when the metal is heated in air but in this case it is contaminated with the nitride, Mg_3N_2, so that it is necessary to moisten the calcined residue with water and re-heat to convert the nitride into oxide, thus—

$$Mg_3N_2 + 3H_2O = 3MgO + 2NH_3 \uparrow$$

On a large scale, the oxide is prepared either by the calcination of magnesite, or from sea water as described on p. 489.

Properties of Magnesium Oxide. Magnesium oxide is a white powder. It is only slightly soluble in water, for example at 20°C, 100 g of water will only dissolve 0·001 g of the oxide. The higher the temperature of calcination the lower the solubility. The dilute solution which is formed is slightly alkaline in reaction.

Magnesia is an extremely stable compound, thus it may be heated to a temperature of 2500°C, without undergoing decomposition. It reacts with acids forming the corresponding magnesium salts.

Uses of Magnesium Oxide. Probably the most important use for magnesia is in the manufacture of refractories; for such applications a dead-burned magnesia is desirable. The oxide is also used for the production of metallic magnesium; for electrolytic production a reactive, caustic magnesia is needed, whilst for thermal reduction processes a fully calcined magnesia is to be preferred. It is also used in the vulcanization of rubber. Other uses include its application as an abrasive for the polishing of metals and alloys, and for medicinal purposes ("Milk of magnesia").

Magnesium Hydroxide, $Mg(OH)_2$, is precipitated as a white gelatinous mass when alkali metal hydroxides are added to the solution of a soluble magnesium salt, thus—

$$MgSO_4 + 2NaOH = Mg(OH)_2 \downarrow + Na_2SO_4$$

This compound is insoluble in excess of the alkali metal hydroxide; it is very slightly soluble in water, being less soluble than calcium hydroxide. It dissolves in solutions of ammonium salts according to the following typical equation—

$$Mg(OH)_2 + 2NH_4Cl \rightleftharpoons MgCl_2 + 2NH_4OH$$

In this system of two mixed electrolytes, magnesium hydroxide is slightly soluble although highly dissociated, whereas ammonium hydroxide is soluble but only slightly dissociated.

Thus, the solid magnesium hydroxide dissolves progressively in order to maintain the dissolved magnesium hydroxide at its saturation value. This process continues until all the solid magnesium hydroxide has disappeared. The reaction is also probably facilitated by the interaction of the ammonium ion with magnesium chloride as follows—

$$NH_4^+ + Cl' + Mg^{++} + 2Cl' = NH_4(MgCl_3)$$

Magnesium hydroxide is a strong base reacting with acids to form magnesium salts, and if heated with chlorine it reacts thus—

$$6Mg(OH)_2 + 6Cl_2 = 5MgCl_2 + Mg(ClO_3)_2 + 6H_2O$$

Insoluble Salts of Magnesium

Magnesium Carbonate, $MgCO_3$. This compound is found in nature as magnesite and as dolomite.

Magnesium carbonate may be prepared by the addition of a solution of sodium bicarbonate to the solution of a soluble magnesium salt; the addition of sodium or potassium carbonate solution instead of the bicarbonate results in the precipitation of the white basic magnesium carbonate, of the general formula, $xMgCO_3 \,.\, yMg(OH)_2 \,.\, zH_2O$, typical examples being

$$3MgCO_3 \,.\, Mg(OH)_2 \,.\, 4H_2O \text{ and } 3MgCO_3 \,.\, Mg(OH)_2 \,.\, 3H_2O$$

If carbon dioxide is passed through a suspension of the basic carbonate a clear solution of *magnesium bicarbonate* is produced, and if this solution is then heated to 50°C, crystals of magnesium carbonate trihydrate are precipitated.

$$MgCO_3 . Mg(OH)_2 + 3CO_2 + H_2O = 2Mg(HCO_3)_2$$

For the same reasons as stated above magnesium salts do not yield a precipitate when treated with ammonium carbonate solution along with ammonium chloride, the magnesium being present in the form of a complex anion, $[MgCl_3]'$. This fact is utilized in the separation of magnesium from the metals of Group 5 in qualitative analysis, i.e. calcium, strontium and barium.

Uses of Magnesium Carbonate. The basic carbonates of magnesium are used extensively in the manufacture of inks, paints and varnishes, in which they are used as "fillers," in tooth powders, and for use with rubber accelerators. Mixed with asbestos they are used for heat-insulating coverings for steam pipes. A special kind of dolomite is used with magnesia for the manufacture of *Vienna lime* for buffing metals. Dolomite is used as a metallurgical flux, and, of course, dolomite and magnesite are the raw materials for the extraction of metallic magnesium.

Magnesium Phosphates. In the cold, a solution of di-sodium hydrogen phosphate reacts with a soluble magnesium salt to produce a precipitate of the slightly soluble compound, *magnesium hydrogen phosphate*, $MgHPO_4 . 7H_2O$. If this compound is suspended in water and the suspension heated, the insoluble normal *magnesium phosphate* is formed along with a soluble acid salt—

$$4MgHPO_4 = Mg_3(PO_4)_2 \downarrow + MgH_4(PO_4)_2$$

If a solution of di-sodium hydrogen phosphate reacts with the solution of a soluble magnesium salt in the presence of ammonium hydroxide and ammonium chloride, a colourless precipitate of *magnesium ammonium phosphate*, $Mg(NH_4)PO_4 . 6H_2O$, is obtained. In ammonium hydroxide solution this compound exhibits only a very slight solubility. The formation of this compound is often applied as a test in qualitative analysis but it is important to note that certain other metals will also form insoluble phosphates of similar constitution. It is therefore necessary to ensure that all such metals are removed before applying the test for magnesium. As well as being employed as a qualitative test for magnesium, the formation of magnesium ammonium phosphate is also used as the basis of one quantitative method for the determination of magnesium. In this case, the precipitate after filtration is heated to a temperature of about 650°–700°C, when ammonia and water are evolved giving *magnesium pyrophosphate* as follows—

$$2[MgNH_4PO_4 . 6H_2O] \rightarrow Mg_2P_2O_7 + 13H_2O \uparrow + 2NH_3 \uparrow$$

Soluble Salts of Magnesium

Magnesium Chloride, $MgCl_2$. This magnesium compound is found as a constituent of certain salt deposits and in sea water. The manufacture of magnesium chloride has already been described on p. 492. In the laboratory magnesium chloride may be prepared by the action of hydrochloric acid on the carbonate. On evaporation of the solution the hexahydrate crystallizes out.

In the air, the hexahydrate deliquesces. It is very soluble in water, being hydrolyzed in aqueous solution. A number of hydrates other than the hexahydrate have been identified. If any of these hydrates are heated at about 200°C in air they lose water and hydrogen chloride, forming magnesium oxychloride, thus—

$$2[MgCl_2 \,.\, 6H_2O] = 11H_2O + [MgO \,.\, MgCl_2] + 2HCl \uparrow$$

On further heating this oxychloride loses chlorine and is converted to magnesia, thus—

$$2[MgO \,.\, MgCl_2] + O_2 \xrightarrow[\text{from the air}]{600°C} 4MgO + 2Cl_2 \uparrow$$

Anhydrous magnesium chloride cannot therefore be prepared by heating the hydrated salt in air. The following are the chief methods available for the production of the anydrous salt—

(*a*) Dehydration of magnesium chloride hexahydrate at a gentle heat in a stream of hydrogen chloride.

(*b*) By passing chlorine over heated magnesium maintained at about 650°C.

(*c*) By heating a mixture of magnesia and carbon at 850°C, in an atmosphere of chlorine (*see* p. 492).

Magnesium Sulphate, $MgSO_4$. This salt occurs in nature as *kieserite*, $MgSO_4 \,.\, H_2O$. In the laboratory, and on a commercial scale, magnesium sulphate is prepared by the action of sulphuric acid on magnesium carbonate or hydroxide. If the hot concentrated solution of this magnesium sulphate is cooled below 25°C, rhombic crystals of the heptahydrate, $MgSO_4 \,.\, 7H_2O$ separate out. This hydrate is known as *Epsom salt*. Other hydrates have also been identified. All the hydrates yield the anhydrous salt when heated to 200°C, and if heated to higher temperatures magnesia results.

Pure magnesium sulphate is used in medicine, less pure material finding application as sizing and as a fireproofing agent. Magnesium sulphate is also used in the tanning trades, for dyestuffs manufacture and the manufacture of soap and paint.

CALCIUM

Occurrence. Calcium is one of the most abundant of all the elements; it is, in fact, the fifth most abundant in the earth's crust. It is far too reactive to occur free in nature and occurs combined with many other elements but chiefly with oxygen, silicon, aluminium and carbon. The most important of these naturally occurring compounds is calcium carbonate; whole geological formations such as chalk and the carboniferous limestone consist almost entirely of calcium carbonate, whilst thick and thin beds of limestone are more or less common throughout entire sets of stratified rocks. Some of the more important of the calcium minerals are enumerated below.

Type of Compound	Name of Mineral and its Formula
Carbonate	Limestone, $CaCO_3$ (also known as chalk) Calcite, $CaCO_3$ (hexagonal) (Dog-tooth spar) Aragonite, $CaCO_3$ (orthorhombic) Dolomite, $CaCO_3.MgCO_3$ Gaylussite, $Na_2CO_3.CaCO_3.5H_2O$
Sulphate	Anhydrite, $CaSO_4$ Gypsum, $CaSO_4.2H_2O$
Phosphate	Apatite, $3Ca_3(PO_4)_2.CaF_2$
Fluoride	Fluorspar, CaF_2

In addition to the above minerals, calcium also occurs in the form of many silicates, such as *anorthite felspar*, $CaO . Al_2O_3 . 2SiO_2$.

Calcium compounds constitute an essential part of plant and animal tissue; thus calcium is found in bones, largely as calcium phosphate.

Extraction of Metallic Calcium

Electrolytic Extraction. Calcium is obtained by the electrolysis of its fused anhydrous chloride. This extraction is usually carried out in a cell of the type introduced by Rathenau in which the cathode is a round steel pipe capable of movement upwards and downwards. The anode material is graphite and this material constitutes the cell lining, in addition auxiliary anodes also of graphite are employed. The cell, the auxiliary anodes and the cathode are all water-cooled; it is necessary to keep the cell temperature down to a minimum otherwise the liberated calcium tends to oxidize.

The electrolyte consists of a fused mixture of calcium chloride and calcium fluoride (six parts of $CaCl_2$ to one part CaF_2 being a common mixture

which melts at 650°C; the melting point of calcium is 851·1°C). In operation the water-cooled cathode is adjusted so that its tip just touches the surface of the electrolyte. The resultant high current density raises the temperature in the neighbourhood of the cathode above the melting point of calcium, causing the metal to be deposited in the molten state. Under these conditions the calcium "wets" the steel cathode to which it adheres when the cathode is raised. The raising of the cathode is carried out slowly so that a vertical stick or "carrot" of calcium is produced. The lower end of the carrot quickly becomes the effective cathode, the steel merely serving as a lead for the current supply. When the cathode has reached the end of its upwards travel, electrolysis is stopped and the calcium carrot removed. The carrots produced from the latest cells vary in size from 7–14 in. diameter and 5–25 in. in length. The carrot is protected from oxidation during the progress of its travel by a layer of solidified electrolyte; thus the calcium content of the carrot is only about 85 per cent. To remove the electrolyte the crude product is melted and cast into various shapes in an atmosphere of argon; the product from this process contains 95–97 per cent calcium. A higher grade metal is produced by distillation of the 95–97 per cent grade in a retort under a high vacuum.

Thermal Reduction of Calcium Oxide. Calcium is also prepared by the thermal reduction of calcium oxide by aluminium under vacuum. The aluminium powder (96–99 per cent pure) is briquetted with lime before charging into horizontal retorts, the ends of which project through the furnace wall, the calcium (98–99 per cent pure) condensing as the solid phase in the cold ends.

Physical Properties of Calcium

(*a*) Calcium is a silvery-white metal.
(*b*) It is a very light metal (density = 1·55).
(*c*) When pure it is so soft that it may be cut with a knife, and unlike sodium or other alkali metals it may be handled without danger.

Chemical Properties of Calcium

(*a*) Calcium is a very reactive metal.
(*b*) On exposure to air it becomes coated with a layer of oxide, hydroxide and carbonate.
(*c*) When gently heated in air it readily takes fire, forming the oxide together with a little calcium nitride, Ca_3N_2.
(*d*) It combines with hydrogen when heated to form the hydride CaH_2.
(*e*) When heated with carbon it reacts to form calcium carbide, CaC_2.
(*f*) With water, calcium reacts to form its hydroxide and liberate hydrogen, thus—

$$Ca + 2H_2O = Ca(OH)_2 + H_2\uparrow$$

(*g*) Calcium reacts vigorously with acids to form calcium salts.
(*h*) Calcium does not react with alkalis.

Uses of Calcium. By reason of its relatively high melting point and its low vapour pressure, calcium is finding increasing use as a deoxidizing agent for such metals as copper, aluminium, magnesium, nickel, and nickel-chromium alloys and special steels. When used as a deoxidant for copper the electrical conductivity is not greatly reduced. Lead-calcium alloys containing about 3 per cent calcium have found application for bearing purposes. Calcium is also employed as a minor addition in other alloys.

Calcium is used in the Betterton process for removing bismuth from lead.

The metal is also used for the manufacture of calcium hydride.

Compounds of Calcium

Calcium Hydride, CaH_2, is prepared by the direct action of hydrogen on metallic calcium heated to approximately 350°C. Calcium hydride is a colourless solid with a density of 1·7. It is acted upon by water with the formation of calcium hydroxide and the liberation of hydrogen, thus—

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2 \uparrow$$

In commerce this compound is often sold under the name of "Hydrolith." It is used commercially to some extent as a means of producing hydrogen in special circumstances and also as a reducing agent for the production of such metals as titanium, vanadium, uranium and zirconium.

Calcium Carbide, CaC_2, is prepared by heating a mixture of quicklime and carbon in an electric furnace at a temperature of approximately 2000°C. The source of carbon is coke, anthracite or charcoal, coke being most commonly used. The chemical reaction involved is—

$$CaO + 3C = CaC_2 + CO \uparrow$$

Two types of electric furnace are employed for the manufacture of calcium carbide; they are (i) ingot furnaces in which the carbon electrode is lowered into the carbon-lined steel box or car until it strikes an arc with the carbon lining. The charge is then added from time to time, and the electrode gradually raised until the furnace is filled. The filled car is then disconnected, cooled, and the ingot removed; and (ii) the tapping furnace which produces molten calcium carbide. This furnace consists of a steel shell lined with carbon, the arc being produced by three electrodes connected to a three-phase supply. The lime and coke are charged continuously and the molten calcium carbide at 1800°C is likewise tapped continuously.

The solidified carbide from either type of furnace is broken up and graded for size in an atmosphere of nitrogen to prevent the possibility

of explosion due to the generation of acetylene which is very likely in ordinary atmospheres.

Properties of Calcium Carbide. Pure calcium carbide is white, but the commercial variety is usually dark grey in colour owing to the presence of impurities. It is a hard, brittle crystalline solid. It reacts with water to produce acetylene as follows—

$$CaC_2 + 2H_2O = C_2H_2 \uparrow + Ca(OH)_2$$

The calcium carbide of commerce is almost entirely consumed by two applications—

(1) Its reaction with water to produce acetylene as described above. Acetylene is employed as a fuel in welding and metal cutting, and also as a raw material in a large number of organic syntheses. For example, a large proportion of the acetic acid is produced by treating acetylene with water in the presence of mercurous sulphate followed by subsequent air oxidation of the acetaldehyde formed initially.

$$\underset{\text{Acetylene}}{CH \equiv CH} + H_2O \xrightarrow{Hg_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{O_2} \underset{\text{Acetic acid}}{CH_3COOH}$$

Acetylene is also employed in the manufacture of the monomers from which vinyl polymers are formed. Similarly, it is the basis of "Neoprene," a synthetic rubber.

(2) It reacts with nitrogen when heated, to form calcium cyanamide $CaCN_2$—

$$CaC_2 + N_2 = CaCN_2 + C$$

Calcium cyanamide is an important fertilizer being known commercially under the name of "Nitro-lime." In the chemical industry calcium cyanamide is used for the production of ammonia, which is prepared by the action of water on calcium cyanamide when heated under pressure in autoclaves.

$$CaCN_2 + 3H_2O = 2NH_3 \uparrow + CaCO_3$$

The use of nitrolime as a fertilizer is probably dependent upon the liberation of ammonia by action with water.

Calcium Oxide, CaO (Lime or Quicklime). Pure calcium oxide may be prepared in the laboratory by heating calcium hydroxide, carbonate or nitrate or by burning metallic calcium in an atmosphere of oxygen.

On a commercial scale lime is prepared by heating or "burning" limestone in kilns. The reaction involved is—

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \uparrow - 43\,250 \text{ cal.}$$

The dissociation pressure of calcium carbonate increases as the temperature rises, being one atmosphere (760 mm) at 890°C. In order to facilitate decomposition of the carbonate it is usual therefore to arrange for carbon dioxide to be drawn off by the suction set up by a draught of air.

For the burning of lump limestones, vertical kilns are almost invariably employed, the firing of such kilns being carried out either by the use of solid fuel such as coal or, in more modern plants, by the use of gaseous fuel such as producer gas. In many plants the gases issuing from the top of the kiln are allowed to escape, but in the ammonia-soda industry the kilns are closed and under slight suction the exit gases are led to compressors and thence to the carbonating towers. Certain plants, particularly those using fines or small size limestones, employ rotary kilns; precipitated calcium carbonate such as that from cauticizing plants can only be burned in rotary kilns.

Properties of Calcium Oxide

(*a*) Calcium oxide is a white amorphous powder.

(*b*) It is very refractory and may be heated to a higher temperature without undergoing any chemical decomposition. It fuses at approximately 2600°C.

(*c*) Calcium oxide may only be reduced to metal in exceptional circumstances (*see* Extraction of calcium by thermal reduction).

(*d*) Calcium oxide is a reactive compound, although when pure and dry it does not react at atmospheric temperature with carbon dioxide, sulphur dioxide, chlorine, hydrogen chloride and nitrogen peroxide.

It reacts with water to form calcium hydroxide; this process is known as the *slaking* of lime.

$$CaO + H_2O = Ca(OH)_2 + 15\,900 \text{ cal.}$$

It will be noted from the above reaction that the process of slaking is accompanied by the evolution of a considerable quantity of heat.

When moist, calcium oxide reacts with acid gases and chlorine, forming calcium carbonate and sulphite with carbon dioxide and sulphur dioxide respectively, and calcium chloride and bleaching powder with hydrogen chloride and chlorine.

When heated with silica, SiO_2, it forms calcium silicates of which the following is typical—

$$CaO + SiO_2 = CaO \,.\, SiO_2$$

The latter reaction is of importance in metallurgical smelting processes in which limestone is added to the furnace charge to remove silica or siliceous gangue as easily fusible silicate slags.

At red heat calcium oxide reacts directly with chlorine to form calcium chloride—

$$2CaO + 2Cl_2 = 2CaCl_2 + O_2$$

(*e*) Calcium oxide is a strongly basic oxide reacting vigorously with acids to form the corresponding calcium salts.

Uses of Lime. Lime is used in the manufacture of bleaching powder and caustic soda and as a constituent of many types of cement and mortar. In the laboratory it finds application as a drying agent in which connexion it is often used as "soda lime." This substance is made either by slaking lime with sodium hydroxide solution and evaporating the solution, or alternatively by adding molten sodium hydroxide to lime. Soda lime has two advantages over sodium hydroxide for which it substitutes as an absorbent of carbon dioxide; they are (*a*) it is not deliquescent, and (*b*) it has a higher melting point. Lime is also used alone as a drying agent for such gases as ammonia which react with other drying agents such as calcium chloride and sulphuric acid.

Calcium Hydroxide, $Ca(OH)_2$ (Slaked Lime). Calcium hydroxide is made by slaking lime with water. Water is sprayed on to lime, when the latter quickly falls to a powder, the excess water being evaporated by the heat of the slaking.

Properties of Calcium Hydroxide

(*a*) Calcium hydroxide is a white powder.

(*b*) It is only slightly soluble in water; thus at 0°C, 100 g of water will only dissolve 0·227 g of the hydroxide; at higher temperatures even less is dissolved—at 10°C, 0·17 g slaked lime, and at 80°C only 0·059 g.

(*c*) The aqueous solution of calcium hydroxide is known as *lime water*; if the solution contains an excess of the solute the resulting suspension is termed *milk of lime*.

(*d*) If carbon dioxide is passed through water a precipitate of calcium carbonate is formed—

$$Ca(OH)_2 + CO_2 = CaCO_3 \downarrow + H_2O$$

If carbon dioxide is then passed through this suspension, the insoluble carbonate is converted to the soluble bicarbonate as follows—

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

The addition of calcium hydroxide to a solution of calcium bicarbonate results in the precipitation of calcium carbonate as follows—

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 \downarrow + 2H_2O$$

This reaction is of considerable importance in water softening since hard waters often contain dissolved calcium bicarbonate.

(*e*) Slaked lime reacts with acid gases and acids forming the corresponding calcium salts—

$$Ca(OH)_2 + SO_2 = CaSO_3 + H_2O$$

(*f*) It reacts with ammonium salts when heated, evolving ammonia—

$$Ca(OH)_2 + 2NH_4Cl = CaCl_2 + H_2O + 2NH_3 \uparrow$$

(*g*) With chlorine, various products are obtained according to the conditions which exist, as follows—

Reaction of Chlorine with Slaked Lime. At atmospheric temperature bleaching powder results as follows—

$$Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O$$

At red heat calcium chloride and oxygen are formed—

$$2Ca(OH)_2 + 2Cl_2 = 2CaCl_2 + 2H_2O + O_2 \uparrow$$

Reaction with Milk of Lime. With cold milk of lime calcium chloride and calcium hypochlorite are produced as follows—

$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(ClO)_2 + 2H_2O$$

With hot milk of lime calcium chlorate and calcium chloride are formed thus—

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$$

Uses of Slaked Lime. In the laboratory, slaked lime is used as an absorbent for gases such as carbon dioxide, chlorine, and acid gases generally. Its reaction in aqueous solution with carbon dioxide is used as a means of detecting this gas.

On a commercial scale, slaked lime is used in the manufacture of bleaching powder, of caustic soda, both by Gossage's process and also in the ammonia-soda process, for the purification of coal gas and sugar, for the manufacture of glass and the making of cements and mortar. It also finds application in the "lime-soda" process for the softening of hard water.

Calcium Carbonate, $CaCO_3$, occurs in nature in a wide variety of forms; the more important are (*a*) *Calcite*, other forms of which are Iceland Spar, Dog Tooth Spar; and (*b*) *Aragonite*. Limestone, marble and chalk contain calcium carbonate in the form of calcite; whilst in coral, calcium carbonate is present in the form of aragonite. Calcite crystallizes in the hexagonal system, whilst aragonite crystallizes in the rhombic system. Calcium carbonate may be prepared in the laboratory by precipitation from the solution of a soluble calcium salt by means of a soluble carbonate; the precipitate is then washed and dried.

Properties of Calcium Carbonate

(*a*) In pure water, calcium carbonate is practically insoluble, but in the presence of dissolved carbon dioxide, calcium carbonate readily dissolves owing to the formation of the soluble calcium bicarbonate, thus—

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

On standing, or if gently heated this solution of calcium bicarbonate

decomposes with the precipitation of calcium carbonate and the production of water and carbon dioxide. This reaction taking place over very prolonged periods of time has led to the formation of stalactites on the roof and stalagmites on the floor of caves.

(*b*) Calcium carbonate is soluble in acids forming the corresponding calcium calts. In this connexion it should be noted that those acids which form insoluble calcium salts lead to the formation of an insoluble skin of the salt on the surface of the calcium carbonate thus slowing down—or even stopping—the attack of the acid. If the calcium carbonate is used in the finely divided form this, of course, does not take place.

Uses of Calcium Carbonate. The uses of this compound include its application as a flux in metallurgical smelting processes; for the manufacture of lime, and for whiting, which is finely ground chalk freed from sandy impurities by washing with water. Whiting mixed with 18 per cent boiled linseed oil in known as "putty." In precipitated form it is employed in the manufacture of tooth pastes and for medicinal purposes and for cosmetics. In the laboratory it is often used as a source of carbon dioxide.

Calcium Bicarbonate, $Ca(HCO_3)_2$, may be obtained as a flocculent white precipitate when a cold aqueous solution of potassium bicarbonate is added to calcium chloride solution cooled in a freezing mixture. On warming the precipitate to atmospheric temperature it decomposes yielding calcium carbonate, water and carbon dioxide.

Calcium Chloride, $CaCl_2$. In the laboratory this compound may be prepared by the action of hydrochloric acid upon calcium carbonate.

In industry it is produced in large quantities as a by-product of the ammonia-soda process for the manufacture of sodium carbonate.

Properties of Calcium Chloride

(*a*) Calcium chloride is very soluble in water; for example, at 0°C, 100 g of water dissolve 60 g of the anhydrous salt, whilst at 100°C, 159 g of the salt may be dissolved.

(*b*) Aqueous solutions of calcium chloride freeze at lower temperatures than 0°C, thus a solution containing 42·5 g calcium chloride in 100 g of water freezes at −55°C.

(*c*) Anhydrous calcium chloride absorbs water to form $CaCl_2 . 6H_2O$; it also reacts with ethyl alcohol to form $CaCl_2 . 2(C_2H_5OH)$, and with ammonia to form $CaCl_2 . 8NH_3$.

(*d*) When heated, the hexahydrate loses four of its molecules of water of crystallization at 200°C, and at higher temperatures is converted to the anhydrous salt. Some calcium oxide is also formed during the last stages of dehydration, thus—

$$CaCl_2 + H_2O \rightleftharpoons CaO + 2HCl$$

Uses of Calcium Chloride. The chief applications of calcium chloride

are in the form of solutions used to lay dust (because it is deliquescent and remains moist), and as a circulating liquid in refrigeration.

The solid salt constitutes the chief constituent of the electrolyte employed for the production of calcium by the electrolytic process. It is used in the laboratory as a drying agent but it cannot be used with ammonia or compounds containing the $-NH_2$ or $-OH$ groups since it forms compounds with such materials. In connexion with its use as a drying agent, care must be taken to ensure that no calcium oxide is present in the anhydrous salt otherwise acid gases will be absorbed.

Calcium Fluoride, CaF_2, occurs in nature in large quantities as fluorspar. When heated to approximately 900°C, calcium fluoride melts to form an opaque, greyish enamel.

It finds considerable application in industry for the "thinning out" of glasses and metallurgical slags. It is also a constituent of glazes and in addition serves as a source of fluorine.

Calcium Sulphate, $CaSO_4$, occurs in nature as anhydrite, $CaSO_4$, and as *gypsum*, $CaSO_4 . 2H_2O$. Other forms of gypsum are selenite, alabaster and satin spar.

In the laboratory the dihydrate may be prepared by the addition of dilute sulphuric acid to an aqueous solution of calcium chloride, thus—

$$CaCl_2 + H_2SO_4 + 2H_2O = CaSO_4 . 2H_2O \downarrow$$

Properties of Calcium Sulphate

(*a*) Calcium sulphate is only slightly soluble in water (2 g/litre) exhibiting a maximum solubility of 2·8 g/litre at 38°C.

(*b*) When heated to 110°–139°, the dihydrate loses three-quarters of its water of crystallization, being converted into the hemi-hydrate,

$$CaSO_4 . \tfrac{1}{2}H_2O \text{ or } 2CaSO_4 . H_2O$$

the chief constituent of plaster of Paris.

If the hemi-dydrate is heated above 200°C the anhydrous salt is produced.

These various changes may be depicted as follows—

$$\underset{\text{gypsum}}{CaSO_4 . 2H_2O} \rightleftharpoons \underset{\text{orthorhombic dihydrate}}{CaSO_4 . 2H_2O} \overset{120°C}{\rightleftharpoons} \underset{\text{plaster of Paris}}{CaSO_4 . \tfrac{1}{2}H_2O} \overset{200°C}{\rightleftharpoons} CaSO_4$$

These changes are reversible, so that when plaster of Paris is mixed with water it sets in a few minutes to form a hard mass with the composition, $CaSO_4 . 2H_2O$. This change is accompanied by a slight expansion. This slight expansion renders plaster of Paris suitable for the making of moulds since detail is thereby accurately reproduced.

When gypsum is heated it first changes into a dimorphous form (orthorhombic dihydrate) of the same chemical composition; this change is

reversible, and it is the re-forming of gypsum that gives rise to the expansion referred to above.

(*c*) The presence of dissolved calcium sulphate in many natural waters gives rise to *permanent hardness*.

Uses of Calcium Sulphate. Calcium sulphate is used as the raw material for the manufacture of plaster of Paris. Parian cement is also a product of the calcination of gypsum; it consists of anhydrous calcium sulphate. It sets very slowly when mixed with water, without suffering expansion, to give a hard, compact mass of gypsum; it is used for the surfacing of floors and for plastering corners of walls which are likely to receive hard wear.

Calcium sulphate is also used for the manufacture of plaster for walls. Some glue and hair are usually added to retard the setting time in order to give the plasterer an opportunity to apply the material.

Calcium Phosphates. Calcium occurs in nature as a number of naturally-occurring phosphates, of which there are two principal varieties—

(1) Apatite, a mineral with a definite composition, $3Ca_3(PO_4)_2 \,.\, CaF_2$, which in a few cases contains chlorine instead of fluorine; and

(2) rock phosphates such as phosphorite, phosphatic limestone, guano, bone beds, etc., which have no definite chemical composition.

One of the chief uses for these materials is as fertilizers, but they also constitute the chief source of elemental phosphorus (*see* p. 669). Phosphate rock, when finely ground has a limited use as a fertilizer on account of its low solubility. Thus, with the object of increasing the solubility it is more usual to convert this material into more soluble forms, such as *superphosphate*, by treatment with sulphuric acid; the following is the probable expression of the main reaction involved in this process of acidulation—

$$\underset{\text{phosphate rock}}{2(CaF)Ca_4(PO_4)_3} + 7H_2SO_4 + 17H_2O \rightarrow \underset{\text{superphosphate}}{3CaH_4(PO_4)_2 \,.\, H_2O} + 2HF + 7(CaSO_4 \,.\, 2H_2O)$$

Another material more concentrated than the ordinary superphosphate is the so-called *triple superphosphate*. This material, which contains 48–50 per cent available P_2O_5 (about three times that present in ordinary superphosphate) is prepared by the action of phosphoric acid on phosphate rock, the reaction involved being—

$$(CaF)Ca_4(PO_4)_3 + 7H_3PO_4 + 5H_2O = \underset{\text{triple superphosphate}}{5CaH_4(PO_4)_2H_2O} + HF$$

A considerable saving in freightage and transportation costs is effected by the use of triple superphosphate instead of the ordinary superphosphate. Phosphorus is also available for use as a fertilizer in the *basic slag* obtained

from basic processes of steel making. This material is chiefly composed of calcium silicophosphate, $Ca_3(PO_4)_3 . CaO . SiO_2$.

Mortar and Cements

Mortar as used by builders is made by mixing slaked lime with sand and water. On standing, the water is lost by evaporation and absorption into the brickwork, whilst the slaked lime is converted, by the action of atmospheric carbon dioxide, into calcium carbonate; the sand acts as a diluent which prevents the mortar from cracking as it sets.

Portland cement is made by mixing and calcining certain types of limestone with clay and sand in a long, horizontally-mounted, rotating furnace termed a "cement kiln." The raw materials are mixed with water to produce a fine sludge or *slurry* which is then fed continuously into the kiln. The kiln is usually heated by means of pulverized coal. The nodules which result from this calcination are cooled and then ground to a very fine powder.

In use, cement is mixed to a paste with water when it undergoes a series of changes which results in the setting of the material to a hard mass exhibiting considerable mechanical strength. The essential constituents of Portland cement are given as follows—

TABLE 85

Essential Constituents of Portland Cement

Formula	Name	Abbreviation
$2CaO . SiO_2$	Dicalcium silicate	C_2S
$3CaO . SiO_2$	Tricalcium silicate	C_3S
$3CaO . Al_2O_3$	Tricalcium aluminate	C_3A
$4CaO . Al_2O_3 . Fe_2O_3$ . . .	Tetracalcium aluminoferrite	C_4AF
MgO	In free state	

It is generally agreed that the hardening of cement takes place by virtue of hydration and of hydrolysis; the following reactions indicate the general trend of the changes involved—

$$C_2S + xH_2O \rightarrow \underset{\text{amorphous}}{C_2S . xH_2O}$$

$$C_3S + xH_2O \rightarrow \underset{\text{amorphous}}{C_2S . xH_2O} + \underset{\text{crystalline}}{Ca(OH)_2}$$

$$C_3A + 6H_2O \rightarrow \underset{\text{crystalline}}{C_3A . 6H_2O}$$

$$C_3A + 3(CaSO_4.2H_2O) + 25H_2O \rightarrow C_3A\,.\,3CaSO_4\,.\,31H_2O$$

$$C_4AF + xH_2O \rightarrow \underset{\text{crystalline}}{C_3A.6H_2O} + CaO.Fe_2O_3.(x-6)H_2O$$

$$MgO + H_2O \rightarrow Mg(OH)_2$$

The relationship of the strength of Portland cement to the constituents is indicated in Table 86.

TABLE 86

Relationship of the Strength of Portland Cement to its Constituents

Compound (*see* Table 85)	Function
C_3A	Responsible for "flash set" (initial set)
C_3S	Responsible for first strength (at 7 to 8 days)
C_2S and C_3S	Responsible for the final strength (at one year)
Fe_2O_3, Al_2O_3, and Mg . .	These render a lower clinkering temperature possible

Concrete is made by mixing cement with gravel or ballast; when mixed with water the pasty mass may then be poured into moulds in which it sets to a hard, rock-like mass. With the object of enhancing the strength, steel rods are often placed in the mould prior to pouring in the concrete; this material is termed *reinforced concrete*.

The material described above is ordinary (or regular) Portland cement, but other varieties are also in production. Thus, *High-Early-Strength* (H.E.S.) cements are made from a material with a high lime-to-silica ratio; they contain a higher proportion of tricalcium silicate than regular Portland cements and hence harden more quickly and with greater evolution of heat; *Chemical* or *Sulphate-Resisting* cements are higher in tetracalcium aluminoferrite and lower in tricalcium aluminate than the regular cements. *High Alumina* cements are made by fusing a mixture of bauxite and limestone; these materials are characterized by a very rapid rate of development of strength and superior resistance to sea water and sulphate-bearing water.

Sorel cement is made by the addition of a strong solution of magnesium chloride to finely ground, caustic calcined magnesia. This material, sometimes known as *magnesium oxy-chloride* cement sets hard in three to four hours; this material is principally used in composition floors, such flooring having the advantage of being non-slip, fireproof, not easily scratched, durable, and capable of taking a wax or oil polish.

Water Treatment and Conditioning

Hard water is a natural water which does not readily give a lather with soap. This *hardness* of certain waters is due to the presence of metallic salts which may be divided into two groups, (*a*) the bicarbonates, and (*b*) the sulphates, chlorides and nitrates. These salts are usually of the metals calcium and magnesium although iron and sodium are also present in some instances.

The bicarbonates give rise to what is known as "carbonate" or *temporary hardness*, which is removed if the water is boiled. On the other hand the sulphates, chlorides and nitrates give rise to *permanent hardness* which is not eliminated by boiling.

There are at present a number of different methods employed on a large scale for water conditioning. They will be described individually below.

Lime-Soda Process. This was the first process to be applied to water conditioning and in its modern application may be divided into, (*a*) the cold lime process, and (*b*) the hot lime-soda process. The calcium ions are removed as calcium carbonate and the magnesium ions as magnesium hydroxide.

For the "carbonate" or temporary hardness the essential reactions are as follows.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O \quad . \quad . \quad . \quad (1)$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3\downarrow + 2H_2O \quad (2)$$

Then since the $MgCO_3$ is fairly soluble—

$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2\downarrow + CaCO_3\downarrow \quad . \quad . \quad (3)$$

For the non-carbonate soluble calcium and magnesium salts the following are the essential reactions—

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2\downarrow + CaCl_2 \quad . \quad . \quad (4)$$

$$CaCl_2 + Na_2CO_3 = CaCO_3\downarrow + 2NaCl \quad . \quad . \quad . \quad (5)$$

$$CaSO_4 + Na_2CO_3 = CaCO_3\downarrow + Na_2SO_4 \quad . \quad . \quad . \quad (6)$$

$$MgSO_4 + Na_2CO_3 + Ca(OH)_2 = Mg(OH)_2\downarrow + CaCO_3\downarrow + Na_2SO_4 \quad (7)$$

The cold lime process in which only lime is used is chiefly of use for partial softening of water for municipal supplies. In this process only reactions (1) to (4) occur.

The hot lime-soda process is chiefly employed for conditioning boiler feed water. Since it is operated at a temperature close to the boiling point of the solution, the reactions proceed faster, the coagulation and the precipitation are facilitated and much of the dissolved gases such as carbon dioxide and air are driven out of solution.

Zeolite Softening Process (also known as the "base-exchange process"). The name *zeolite* is a name applied to a class of complex, hydrated alumino-silicates which contain easily exchangeable ions such as sodium and potassium, hence the name *base-exchange*. During this softening process the calcium and magnesium ions are removed from the hard water by the zeolite and replaced in the water by sodium and/or potassium. This process of water conditioning is, therefore, essentially a cation-exchange process.

The following are typical reactions for the changes occurring during water conditioning, the symbol Ze representing a zeolite.

$$Ca(HCO_3)_2 + Na_2Ze = CaZe + 2NaHCO_3 \quad . \quad . \quad (8)$$

$$CaCl_2 + Na_2Ze = CaZe + 2NaCl \quad . \quad . \quad . \quad (9)$$

Corresponding reactions occur in respect of magnesium compounds.

After a time the zeolite becomes exhausted and has to be regenerated; this is done by passing a strong solution of sodium chloride through the softening plant when the following reaction occurs—

$$CaZe + 2NaCl \text{ (in excess)} = Na_2Ze + CaCl_2 \quad . \quad . \quad (10)$$

During regeneration the effluent containing dissolved calcium chloride is allowed to flow to waste.

Demineralization or Deionizing Process. In addition to the zeolites described above there are now available ion-exchange materials which will remove completely all the dissolved salts from naturally occurring water. These ion-exchange materials may be divided into two groups; (i) cation exchangers; and (ii) anion exchangers.

The cation exchangers are chiefly of organic origin and are either sulphonated natural organic materials or synthetic organic resins containing active sulphonic groups and derived from phenol-formaldehyde or polystyrene resins. They contain an exchangeable hydrogen ion and may be designated as H_2Z. When water containing soluble salts is passed through such a cation-exchange material reactions take place of which the following are typical—

$$H_2Z + CaSO_4 = CaZ + H_2SO_4 \quad . \quad . \quad . \quad (11)$$

$$H_2Z + MgCl_2 = MgZ + 2HCl \quad . \quad . \quad . \quad (12)$$

$$H_2Z + Ca(HCO_3)_2 = CaZ + 2H_2O + 2CO_2 \quad . \quad . \quad (13)$$

where Z represents the ion-exchange material insoluble in water.

Since acidic water is undesirable for most purposes the effluent from cation-exchange treatment is either neutralized, or if demineralization is required, is passed through an anion-exchange material. Such materials consist largely of condensation products of amines with formaldehyde.

The acid removal may be either an absorption of the total acid considered as a molecule—

(*a*)
$$\underset{\text{anion-exchange material}}{R_3N} + HCl = R_3N\,.\,HCl \quad . \quad . \quad . \quad (14)$$

or an anion exchange, as indicated below for a hydroxide-regenerated anion exchanger in the form of a quaternary ammonium base.

(*b*)
$$\underset{\text{anion-exchange material}}{R_3N\begin{matrix}H\\OH\end{matrix}} + HCl = R_3N\begin{matrix}H\\Cl\end{matrix} + H_2O \quad . \quad . \quad (15)$$

Since the cation-exchanger possesses a limited capacity for hydrogen exchange, regeneration is necessary from time to time. This is carried out

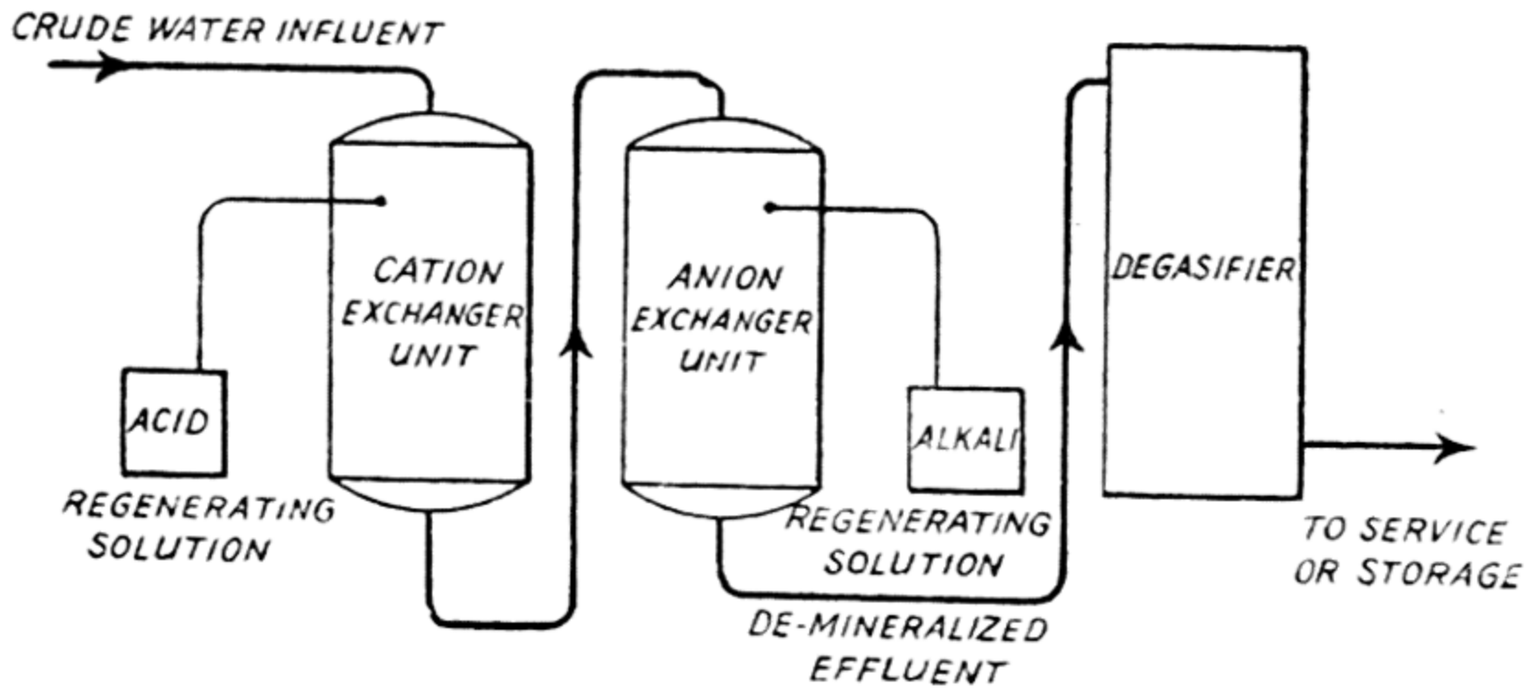


FIG. 166. Diagrammatic Layout of Plant for Demineralization of Water

by passing a solution of hydrochloric acid through the material; the calcium, magnesium and sodium ions held by the material are thus expelled and replaced by fresh replaceable hydrogen ions. The effluent during this process of regeneration is allowed to flow to waste. The reaction during regeneration is as follows—

$$CaZ + 2HCl = H_2Z + CaCl_2 \quad . \quad . \quad . \quad (16)$$

Alternatively sulphuric acid may be used instead of hydrochloric acid. In a similar manner regeneration is necessary in the case of the anion-exchanger, but in this case regeneration is carried out by passing a solution of sodium carbonate through the anion exchange material when the following reaction occurs—

$$2(R_3N\,.\,HCl) + Na_2CO_3\ (\text{excess}) = 2(R_3N) + 2NaCl + H_2O + CO_2 \quad . \quad (17)$$

This double treatment thus deionizes the water and this process is now used as a means of producing water which is comparable with distilled water in respect of dissolved solids. The general layout of the plant is shown in Fig. 166.

Phosphate Conditioning. Sodium hexametaphosphate, $(NaPO_3)_6$, also known as "Calgon," is capable of softening water by reason of the fact that it forms soluble complexes with calcium, magnesium, iron and aluminium and thus prevents the formation of scale when the phosphate is present in excess and when the water is not too hot. These characteristics have led to the so-called "threshold treatment" of water by the addition of as little as half to five parts per million of this hexametaphosphate.

STRONTIUM

Occurrence. The chief minerals of strontium are the sulphate and carbonate; these are—

Celestine, $SrSO_4$, mined at Yate in Gloucestershire; and *Strontianite*, $SrCO_3$, the most important deposits being found in Westphalia.

Extraction and Properties of Strontium. Strontium is extracted either by electrolysis of the fused chloride, or alternatively by the thermal reduction process using metallic aluminium as reducing agent; this is followed by re-distillation at 1000°C. In this latter process the metal has a purity of 99·6 per cent strontium.

Strontium is yellowish in colour and resembles calcium in many of its properties, although in general it is more reactive than calcium. Uses of strontium include its application for the de-oxidation of copper and to promote sound castings. It also finds application as a minor constituent in a number of non-ferrous alloys.

Strontium has a wide variety of uses, especially in the beet-sugar industry, in the manufacture of fireworks, flares, torches and signals in which the brilliant crimson flame characteristics of strontium and its compounds are desired, and to a minor extent for pharmaceutical purposes.

Strontium Hydroxide, $Sr(OH)_2$, is a moderately strong base which reacts with sucrose to form an insoluble compound, thus the recovery is made possible of much sucrose from beet molasses containing considerable proportions of uncrystallizable invert sugar.

Strontium Carbonate, $SrCO_3$, is used in the manufacture of certain special glasses.

BARIUM

Occurrence. The chief minerals of barium are—

Barytes (or *Heavy spar*), $BaSO_4$, found in Derbyshire and in Virginia (U.S.A.); *Witherite*, $BaCO_3$, found near Hexam in Northumberland.

Extraction, Properties and Uses of Barium. Barium is usually extracted by the Guntz process in which barium oxide (3 parts) is heated with aluminium (1 part) to a temperature of approximately 1200°C, under a high vacuum. Sometimes, instead of aluminium, ferrosilicon is employed when a slightly higher temperature, 1250°C, is needed.

Barium when pure exhibits a white metallic lustre, although when contaminated with nitride it has a yellowish appearance. It is malleable and is about as hard as sodium. It is a very reactive metal, being spontaneously inflammable in moist air and in hydrogen. It tarnishes rapidly in dry carbon dioxide and when heated readily burns with a brilliant green flame to the oxide, BaO.

The metal finds application in the radio industry where it is used to clean up the last traces of gas in vacuum tubes. The ternary alloys of lead, calcium and barium are employed as bearing alloys. These alloys are usually prepared by electrolysis of the fused chlorides using a cathode of molten lead.

Compounds of Barium

Oxides. Barium forms two oxides, the *monoxide*, BaO and the *peroxide*, BaO_2. Barium monoxide is best made by heating the hydroxide or the nitrate at red heat. It may also be prepared by heating the carbonate but in this case the carbonate should be mixed with a little charcoal to facilitate the decomposition—

$$BaCO_3 + C = BaO + 2CO \uparrow$$

Barium monoxide is a white powder which slakes on contact with water, a considerable quantity of heat being evolved.

If barium monoxide is heated in air at a temperature of 450–500°C, barium peroxide, BaO_2, is produced; the reaction involved is as follows—

$$2BaO + O_2 \rightleftharpoons^{\text{in air}} 2BaO_2 + 24{\cdot}2 \text{ cal.}$$

This reaction, which is reversible, was the basis of the now obsolete Brin's process for the manufacture of oxygen (*see* p. 380). In this reaction the formation of barium peroxide is favoured by an increase in pressure. Barium peroxide may also be formed as its octahydrate when hydrogen peroxide is added to a cold, saturated solution of barium hydroxide, crystals of the octahydrate, $BaO_2 . 8H_2O$, may be separated from the solution. The thermionic emission of radio valve filaments is appreciably increased by coating them with barium oxide.

Barium Hydroxide, $Ba(OH)_2$, is obtained when the oxide is slaked. It is a white powder which, unlike calcium hydroxide, can be fused without undergoing decomposition. It has a higher solubility in water than either calcium or strontium hydroxide. Its aqueous solution is alkaline in reaction and is known as *baryta water*. Baryta water is used in volumetric analysis for the titration of acids and is of value since the solution is always free from dissolved carbonate owing to the insolubility of this compound.

Barium Salts. Two general methods are employed for the preparation of barium salts, they are—

(*a*) from barium carbonate by the action of the appropriate acid;

(*b*) from barium sulphate either by fusion with excess sodium carbonate followed by treatment as under (*a*), or alternatively, by strongly heating with carbon to form barium sulphide which is then dissolved in the appropriate acid.

Barium Sulphate, $BaSO_4$. Used extensively in the manufacture of the pigment, "lithopone," and in the finely divided state as an extender in paints, it is also used as a loader for paper, soap, rubber and linoleum. A recent and increasingly important use is as a heavy medium in muds which are poured into oil-wells to hold back gas during boring operations until the casings are inserted.

Precipitated Barium Sulphate or *blanc fixe* is whiter and finer-grained than the powdered barytes. Blanc fixe is largely used as a base for dye-stuffs, as a filler in enamel paints and for coating paper. Barium sulphate, being insoluble and opaque to X-rays, forms an important constituent of the "barium meal" which is given to patients previous to radiographing the internal digestive organs.

Barium Sulphide, BaS, is prepared by the reduction of barium sulphate with carbon. It reacts readily with water, forming the hydroxide and the hydrosulphide, thus—

$$BaS + 2H_2O = Ba(OH)_2 + Ba(HS)_2$$

The chief use of barium sulphide is in the preparation of *lithopone*, an intimate mixture of barium sulphate and zinc sulphide, both compounds being co-precipitated as follows—

$$BaS + ZnSO_4 = BaSO_4 \downarrow + ZnS \downarrow$$

Lithopone is an extremely important paint pigment. Unlike white lead, for which it is often substituted, lithopone is non-poisonous and is not discoloured by the presence of sulphurous gases. Lithopone is also employed as a filler in the manufacture of rubber, linoleum, oilcloth and paper.

THE METALS OF GROUP IIb

The metals of Group II*b* of the Periodic Classification are related to the alkaline earths in the same way as the Coinage metals are allied to the Alkali metals. Magnesium in Group II*a* and zinc in Group II*b* have many properties in common.

Beryllium and magnesium may be regarded as a link between the Zinc group and the Alkaline earth group.

ZINC

Occurrence. The chief source of world's supply of zinc is the mineral *zinc blende*, ZnS, also known as *sphalerite*, but two other minerals, *calamine*, $ZnCO_3$ (also known as *smithsonite*), and *hemimorphite*,

$2ZnO \cdot SiO_2 \cdot H_2O$, make important contributions to the world's supply of zinc metal. These three minerals usually occur in association with lead minerals, particularly galena—naturally occurring lead sulphide. Thus both zinc and lead minerals are mined together, and many of the most productive zinc mines are also the most productive lead mines. Such zinc–lead ores are mined at the Sullivan Mine in British Columbia, Broken Hill (New South Wales), the Bawdwin mines in Upper Burma, and the mines in the Oklahoma region of the U.S.A.

Extraction of Zinc

Zinc is extracted both by pyrometallurgical and by electrolytic methods.

Pyrometallurgical or Thermal Method. The original process for the extraction of zinc was a thermal one and is still employed to a large extent today. In the thermal reduction process the roasted or calcined ore is reduced by strongly heating with carbon in retorts, and the zinc is formed as a vapour which is condensed and collected in receivers outside the reduction furnace.

In the case of sulphide ores the material, after initial crushing, is treated by differential flotation in order to eliminate as far as possible the galena which is almost invariably present. The concentrate thus obtained is roasted when the following reaction occurs—

$$2ZnS + 3O_2 = 2ZnO + 2SO_2 \uparrow$$

The exhaust gas from the roaster, containing about 6 per cent sulphur dioxide is withdrawn by suction, purified and usually converted into sulphuric acid in a Contact Sulphuric Acid plant.

Ores other than sulphide ores are calcined in mechanically operated furnaces. Thus, all ores whether sulphide or non-sulphide, are first converted to zinc oxide.

This zinc oxide is then reduced by strongly heating with carbon in retorts; the metallic zinc is formed as a vapour which is condensed and collected in receivers outside the reduction furnace. Two types of reduction process are employed at the present time. They are (*a*) the horizontal process, and (*b*) the vertical process. The former is the older of the two processes and is of the batch-type operation. Vertical reduction is carried out continuously.

In the older horizontal process the zinc oxide mixed with anthracite is heated in retorts made of fireclay of oval cross-section, being about 5 ft long, 11 in. wide and 8 in. from top to bottom. The retorts are heated by the combustion of producer gas, a temperature of 1400°–1450°C being obtained. Each furnace or bank contains from 380 to 400 such retorts arranged in three or four tiers. Attached to the mouth of each retort a fireclay condenser is luted, whilst at the extremity of the condenser a prolong made of sheet steel is attached (*see* Fig. 167). On heating, the

zinc distils from the retort and is collected in the condenser; the reaction involved is

$$ZnO + C \rightleftharpoons Zn + CO\uparrow$$

Since this reaction is reversible it is necessary to use an excess of carbon, and also to ensure the ready removal of the zinc. The liquid zinc is then ladled into moulds to produce slabs of crude zinc. This material is known as "*spelter*." Since the boiling points of cadmium and zinc are 767°C and 907°C respectively any cadmium present in the ore along with the zinc will distil over in the first fractions of the distillate and so may be removed.

In the vertical retort process the roasted zinc concentrates are briquetted with a bituminous coal of high coking qualities together with a little sulphite lye and clay to serve as binders. The briquettes are then coked at a

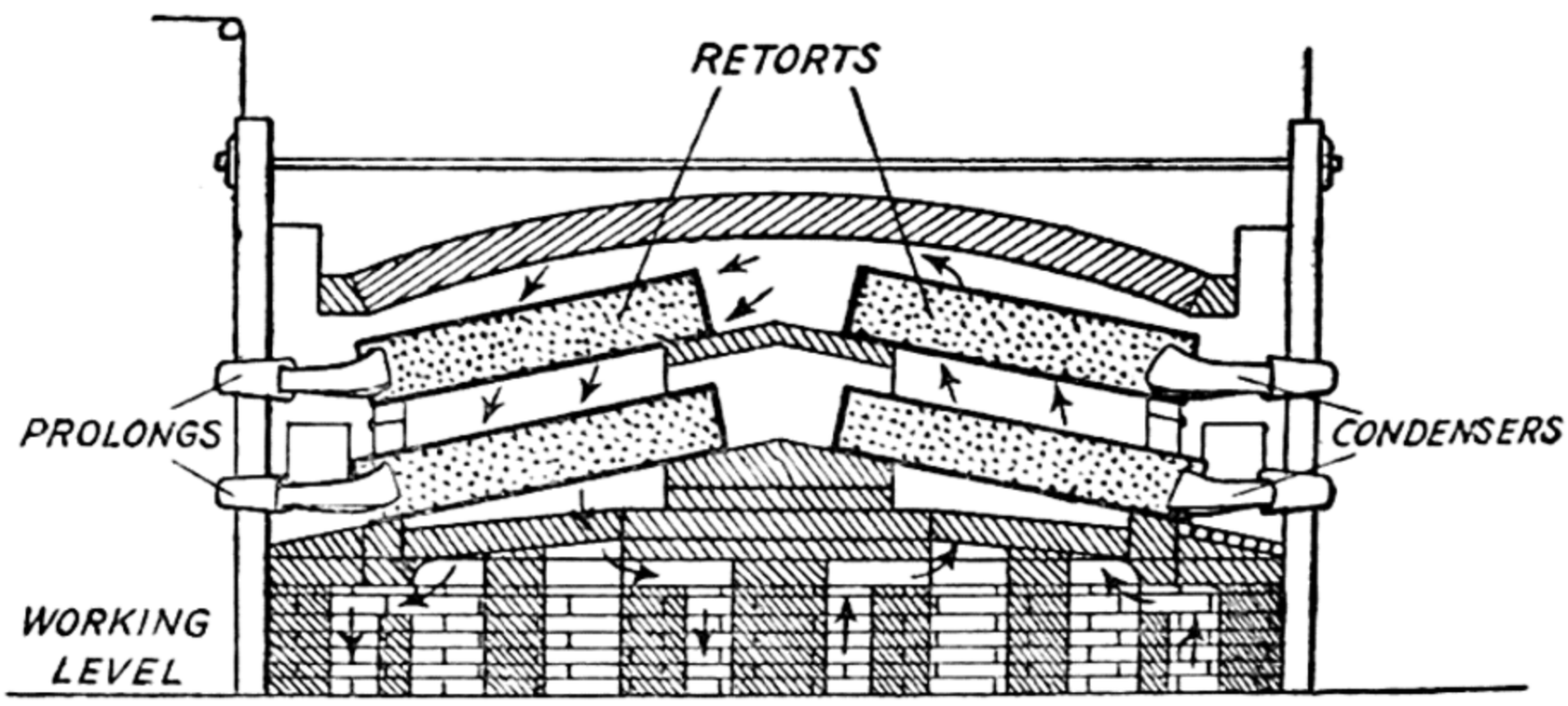


FIG. 167. Distillation of Zinc

temperature of approximately 800°C, the red-hot briquettes then being transferred to the top of the vertical retorts. Each vertical retort consists essentially of a tower having an inner carborundum chamber of cross section 7 ft by 1 ft, in a silica brick combustion setting; each retort has an upper portion 14 ft 6 in. high which is unheated, the lower portion, for a height of 27 ft 6 in., being heated by the combustion of producer gas. Reduction of the zinc occurs at temperatures above the boiling point of the metal and the zinc passes through downcomers into sumps from which it is tapped off at six-hourly intervals. The product is of 99·7 per cent zinc content. This zinc is then separated from cadmium, iron and lead by fractional distillation. Resulting from this process a product having 99·99 per cent zinc content may be obtained.

Electrolytic Method. In this method the crude ore is roasted as in the case of the thermal method; the ore is then leached with dilute sulphuric acid. The resulting solution is purified from such elements as copper, cobalt, iron, antimony and arsenic by treatment with powdered zinc and with ferric hydroxide. The solution of purified zinc sulphate is then electrolyzed in large concrete tanks lined with lead or with rubber. The

anodes are of chemically pure lead, the cathodes of aluminium. The electrolyte is worked at a temperature of 35°–45°C, and a cell voltage of 3·25–3·5 volts maintained at a current density of 30–40 amp/ft². The zinc is stripped from the aluminium cathodes and then melted down to give a material of high purity, 99·99 per cent zinc.

The chief chemical reactions occurring in the electrolytic process are as follows—

Roasting $2ZnS + 3O_2 = 2ZnO + 2SO_2 \uparrow$

Leaching $ZnO + H_2SO_4 = ZnSO_4 + H_2O$

Electrolysis $2ZnSO_4 + 2H_2O = 2Zn + 2H_2SO_4 + O_2 \uparrow$

The electrolytic process is particularly suited for recovery of the metal from complex zinc ores.

Physical Properties of Zinc

(*a*) Zinc is a white metal with a bluish tinge, it has a bright metallic lustre on a freshly fractured surface and is capable of taking a high polish.

(*b*) It has both a low melting point (419·5°C) and a low boiling point (907°C).

(*c*) It is a relatively poor conductor of electricity and heat, being only about one-quarter that of silver in each case.

(*d*) Zinc is soft enough to be marked with a knife.

(*e*) At ordinary temperatures it is not malleable or ductile, but between 110° and 150°C, it may be worked readily, rolled into thin sheet or drawn into wire. At temperatures in excess of 150°C, it loses its workability again.

Chemical Properties of Zinc

(*a*) In dry air at atmospheric temperature zinc is very stable, but if heated it takes fire at about 500°C, burning with a greenish-blue flame to form zinc oxide, ZnO.

(*b*) In moist air, zinc slowly tarnishes owing to the formation of a film of basic carbonates; this film is adherent and protects the metal from further attack.

(*c*) At the boiling point of water, pure zinc is only attacked slowly, but at red heat the metal readily decomposes steam thus—

$$Zn + H_2O = ZnO + H_2 \uparrow$$

(*d*) Zinc combines directly with the halogens and with nitrogen to form zinc nitride, Zn_3N_2. This latter compound is also prepared by heating zinc in a stream of ammonia gas. Zinc does not combine directly with hydrogen or carbon.

(*e*) Commercial zinc, that is zinc containing small amounts of impurities, dissolves readily in dilute acids, but high-purity zinc is only attacked

slowly. The purity of a specimen of zinc may thus be judged by rate of dissolution. Hydrogen is evolved when either sulphuric acid or hydrochloric acid is used, but when nitric acid is employed a gaseous mixture of nitric oxide, nitrous oxide and ammonia is evolved, the proportions differing according to the strength of the acid.

The ready manner in which impure specimens of zinc dissolve in dilute acids is due to the establishment of galvanic couples between the impurities and the zinc.

Concentrated sulphuric acid attacks zinc with the evolution of hydrogen sulphide and the precipitation of sulphur.

(*f*) Because of the liberation of nascent hydrogen in the presence of dilute hydrochloric or sulphuric acids, zinc is a very good reducing agent.

(*g*) Zinc reacts with aqueous solutions of potassium or sodium hydroxides to form soluble zincates, thus—

$$Zn + 2NaOH = \underset{\text{sodium zincate}}{Na_2ZnO_2} + H_2 \uparrow$$

These reactions with caustic alkalis are sometimes used as a means of providing hydrogen.

(*h*) Zinc is a strongly electropositive metal and will therefore displace many other metals from aqueous solutions of their salts. This fact is of considerable industrial importance in connexion with the extraction of copper (*see* p. 457), and the extraction of silver (p. 469) and gold (p. 480).

Uses of Metallic Zinc. The most important property of zinc to which the bulk of its application is due, is its comparatively high resistance to corrosion. It is thus widely employed for the protection of iron and of mild steel.

Galvanized sheets are made by (*a*) hot-dipping, (*b*) metal spraying, and (*c*) electrodeposition. In hot-dipping the mild steel sheets are pickled in acid (usually hydrochloric acid) and then immersed in molten zinc; after withdrawal from the bath the superfluous zinc is removed by passing through rolls. The zinc crystallizes on the surface of the mild steel in the form of large polygonal grains or "spangles." In metal spraying a very fine mist of molten zinc droplets is sprayed by means of a special type of pistol on to the surface of the mild steel. Electrodeposited coatings of zinc are deposited from the sulphate solution in a similar manner to that employed for the electrolytic extraction of zinc.

Iron and steel articles are also coated with zinc by means of the process known as "Sheradizing" in which the clean and scale-free articles are packed in a rotating drum with zinc dust. The drum and its contents are heated to a temperature of about 300°–400°C, for a period of several hours. Under these conditions, although below the melting point of zinc, a firmly-adherent coating of zinc is obtained on the ferrous article. Zinc

is also used in the form of electrodeposited coatings on articles made in various alloys.

Other important applications of zinc are for the manufacture of brasses (copper-zinc alloys), and, in the pure form, for the manufacture of zinc-base die casting alloys; these latter alloys of which the following composition is typical—4 per cent zinc, 2·7 per cent aluminium, balance zinc—exhibit excellent shock resistance and ductility, and also are of a lower cost than either aluminium-base or magnesium-base alloys. Zinc-base alloys constitute about 65 per cent of all die castings used in automobiles; they are also used in the fabrication of domestic and office appliances.

Other uses for zinc include its application to the manufacture of zinc compounds and for making zinc sheet for dry batteries.

Granulated zinc is made by pouring a stream of molten zinc into cold water. Since this form is convenient for weighing and also since it has a large surface area it is the form of the metal most commonly used in the laboratory.

Zinc dust (also known as *zinc grey* or *blue powder*) is prepared by allowing molten zinc to run in small streams through holes in the bottom of a graphite crucible, where it is immediately caught by a blast of compressed air, atomized, and blown into a settling chamber. The particles of zinc are cooled so rapidly that very little oxidation occurs. The fineness of the dust is controlled by air pressure, size of the stream of molten zinc, and the design and location of the stream with respect to the air nozzle.

On a commercial scale zinc dust is used as a precipitant in electrolytic processes of zinc extraction, for Sheradizing and as a metallic pigment in certain types of paint. The metal content of zinc dust averages upwards of 95 per cent zinc, the remainder being oxide.

Compounds of Zinc

Zinc Oxide, ZnO (Zinc white or Philosopher's wool). In the laboratory zinc oxide may be prepared by heating the metal in air, or by heating the hydroxide, the carbonate or the nitrate. On a commercial basis zinc oxide is prepared either by the direct oxidation of volatilized zinc, or alternatively from the ore which is roasted and reduced in the manner described for the thermal extraction process, but instead of collecting the zinc, the vapour is oxidized, the oxide being collected.

Properties of Zinc Oxide

(*a*) Zinc oxide is a white powder which on heating changes to a yellow colour. It reverts to a white colour on cooling.

(*b*) The oxide is readily reduced to metal by heating with carbon at red heat.

(*c*) It reacts with moisture and carbon dioxide when exposed to the atmosphere.

(*d*) It is practically insoluble in water.

(*e*) With acids, zinc oxide forms zinc salts.

(*f*) It also reacts with alkalis forming zincates, thus—

$$ZnO + 2NaOH = \underset{\text{sodium zincate}}{Na_2ZnO_2} + H_2O$$

Zinc oxide may therefore be classified as an *amphoteric oxide*.

(*g*) When zinc oxide is heated with cobalt nitrate, a solid solution of cobalt zincate $CoZnO_2$ in zinc oxide is formed. This solid solution has a characteristic green colour. Its formation is used as a test for the presence of zinc in the charcoal block test for zinc. This green pigment is known as *Rinman's Green*.

Uses of Zinc Oxide. Zinc oxide is an important white pigment; it is regarded as the truest white that can be obtained and, in addition, its colour is unaffected by the gases of the atmosphere.

It is used in the manufacture of glasses which must exhibit a low solubility in water, in hydrochloric acid and in sodium carbonate; it is also used in the manufacture of certain types of porcelain. Other applications include its use as a filler in the manufacture of rubber and, because of its antiseptic qualities, as a constituent of ointments.

Zinc Hydroxide, $Zn(OH)_2$, is obtained as a white precipitate when a solution of either sodium or potassium hydroxide is added to the solution of a soluble zinc salt.

$$Zn^{++} + 2(OH)' \rightarrow Zn(OH)_2 \downarrow$$

An excess of the caustic alkali must be avoided otherwise the insoluble zinc hydroxide will react to form the soluble zincate.

Properties of Zinc Hydroxide

(*a*) Zinc hydroxide is a white powder which is almost insoluble in water.

(*b*) It reacts with acids to form the corresponding zinc salts.

(*c*) With sodium and potassium hydroxide solutions it reacts to form soluble zincates, thus—

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

The hydroxide thus exhibits amphoteric properties like the oxide.

(*d*) In ammonium hydroxide zinc hydroxide also "dissolves," but not to form a soluble zincate; instead the complex cation, $[Zn \,.\, 4NH_3]^{++}$ is formed.

It is to be noted here that although ammonium hydroxide may be employed to precipitate zinc hydroxide from the aqueous solution of a zinc salt, such precipitation will not occur if an ammonium salt is present

along with the ammonium hydroxide. The reason for the absence of precipitate is because (i) the common ion effect reduces the effective concentration of $(OH)'$ ions, and (ii) the zinc is removed to large extent as the complex ions $[Zn \cdot 4NH_3]^{++}$, with the result that the solubility product of zinc hydroxide is not attained, and therefore, zinc hydroxide is not precipitated. On the other hand the concentration of zinc ions Zn^{++} is sufficiently high to allow the precipitation of zinc sulphide when hydrogen sulphide is passed through such a solution since the solubility product of zinc sulphide is lower than that of zinc hydroxide. These facts are of importance in the separation of zinc from other metals in qualitative analysis.

Zinc Salts

Zinc only forms one series of salts and these in general are colourless and readily soluble in water.

Zinc Carbonate, $ZnCO_3$ (Calamine). This compound may be prepared in the laboratory by adding an aqueous solution of sodium bicarbonate to the solution of a soluble zinc salt, thus—

$$Zn^{++} + 2(HCO_3)' \rightarrow ZnCO_3 \downarrow + H_2O + CO_2$$

If instead of sodium bicarbonate, the normal carbonate is employed the precipitate will consist of basic zinc carbonate, $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$; other basic carbonates are also known.

Zinc carbonate is a white powder which readily decomposes on heating. Zinc carbonate finds application for manufacture of preparations for the treatment of the skin, for example *calamine lotion*, (1 g zinc carbonate, 5 ml lime water, 12 ml glycerine and 30 ml water).

Zinc Chloride, $ZnCl_2$ (Butter of Zinc). Hydrated zinc chloride may be obtained by the action of hydrochloric acid upon zinc, or its oxide, hydroxide or carbonate; evaporation of the resulting solution gives rise to the separation of crystals of the monohydrate, $ZnCl_2 \cdot H_2O$.

The anhydrous salt may be obtained by passing either chlorine or hydrogen chloride over heated zinc. Alternatively, the hydrated salt may be dehydrated by heating in a stream of chlorine or of hydrogen chloride.

Properties of Zinc Chloride

(*a*) Anhydrous zinc chloride is a white, very deliquescent solid.

(*b*) It is very soluble in water, at 20°C 350 g of the salt dissolving in 100 g of water.

(*c*) In addition to the monohydrate, other hydrates are known.

(*d*) On heating the hydrated salt the oxychloride is formed, thus—

(i) $$ZnCl_2 \cdot H_2O = ZnCl_2 + H_2O \uparrow$$

(ii) $$ZnCl_2 + H_2O \rightleftharpoons Zn(OH)Cl + HCl \uparrow$$

At higher temperatures zinc oxide is also formed.

Uses of Zinc Chloride. Zinc chloride is employed as a catalyst and as a dehydrating agent in organic chemistry. A solution of zinc chloride made by dissolving the metal in hydrochloric acid, some free acid remaining, is known as *killed spirits* and finds application as a flux in soft soldering. It is also used as a wood preservative.

Zinc Sulphate, $ZnSO_4$ (White Vitriol or Zinc Vitriol). In the laboratory zinc sulphate may be prepared by the action of sulphuric acid upon the metal, or upon its oxide, carbonate or hydroxide. The solution obtained is evaporated and the heptahydrate, $ZnSO_4 . 7H_2O$ is obtained.

On a commercial scale zinc blende is roasted, the concentrate being leached with dilute sulphuric acid. The resulting solution is then evaporated to obtain the hydrate as indicated above.

Properties of Zinc Sulphate

(*a*) Zinc sulphate is very soluble in water, 138 g $ZnSO_4 . 7H_2O$ dissolving in 100 g of water at 10°C.

(*b*) The heptahydrate is isomorphous with the heptahydrated sulphates of iron, nickel, cobalt, cadmium, magnesium, manganese and chromium. Zinc shares with these metals the ability to form double sulphates of the type $K_2SO_4 . ZnSO_4 . 6H_2O$.

(*c*) When the heptahydrate is heated it first loses six of its molecules of water of crystallization at 100°C; at 450°C it is converted to the anhydrous salt, and at still higher temperatures it is converted to zinc oxide with the evolution of sulphur dioxide and oxygen.

$$ZnSO_4 . 7H_2O \xrightarrow{100°C} ZnSO_4 . H_2O + 6H_2O \xrightarrow{450°C} ZnSO_4 + H_2O$$
$$\xrightarrow{740°C} ZnO + SO_2 \uparrow + \tfrac{1}{2}O_2 \uparrow$$

Uses of Zinc Sulphate. The principal use for zinc sulphate is in connexion with the manufacture of lithopone (*see* p. 516). Other uses include its use in medicine, as a disinfectant and as a mordant in dyeing processes.

Zinc Sulphide, ZnS. In the laboratory zinc sulphide is precipitated by passing hydrogen sulphide through an alkaline solution of a zinc salt, or by the addition of ammonium sulphide to a solution of a zinc salt. Alternatively, the solid salt may be prepared by heating either zinc or zinc oxide with sulphur.

Although zinc sulphide is insoluble in water and in organic acids, it is acted upon by mineral acids with the formation of the corresponding zinc salts and the liberation of hydrogen sulphide. Although the pure sulphide in not phosphorescent, traces of impurities (particularly manganese or copper) cause the development of phosphorescence. This characteristic leads to the use of such zinc sulphide for the manufacture of luminous paints. It is also used as a pigment in general paint manufacture.

CADMIUM

Occurrence and Extraction. Cadmium is the rarest of the common metals. The only cadmium mineral of importance is the yellow sulphide *greenockite*, CdS, but this never occurs in sufficient quantities to render it workable. Thus, all the cadmium of commerce is obtained as a by-product in the treatment of zinc ores, in which it is present as the sulphide in intimate association with zinc blende. But even in such zinc ores the content of cadmium is small, rarely being as much as 0·5 per cent. In the world's most productive zinc and cadmium ore field, namely the Tri-State region of Oklahoma, Kansas and Missouri in the U.S.A., the ores average only about 0·3 per cent cadmium.

The cadmium-containing zinc obtained in the thermal reduction of zinc ores is subjected to fractional distillation when, because of the different boiling points of cadmium (767°C) and zinc (907°C), the two metals are separated one from another. In this fractional distillation, fractionating columns are employed, each about 48 ft high. The linings of these columns and retaining trays are made of carborundum.

Properties and Uses. Cadmium is a metal exhibiting a tin-white colour. It is soft metal. It has a low melting point (320·9°C) and a low boiling point (767°C). It is stable in dry air, but in moist air it becomes coated with oxide and carbonate. It dissolves in acids to form the corresponding cadmium salts. It is less electropositive than zinc and therefore zinc will precipitate cadmium from solutions of its salts. It differs from zinc and resembles mercury in that (*a*) it can form univalent compounds (e.g. Cd_2O), (*b*) its hydroxide is not amphoteric, (*c*) its halides are non-deliquescent, (*d*) its sulphate, $3CdSO_4 . 8H_2O$ is not a vitriol.

Cadmium is used as an electrodeposited coating, and also as a metal sprayed coating for the protection of small steel articles such as nuts, bolts and locks.

Cadmium is also used to a limited extent as a de-oxidizer in the melting of aluminium, silver and nickel alloys. It is also a major constituent in a number of low melting-point alloys, (e.g. Wood's metal, 50 per cent Bi; 12·5 per cent Cd; 25 per cent Pb; 12·5 per cent Sn, which melts at 65°–68°C).

Recently cadmium, in the form of rods, has been used in the atomic pile to retard the reaction by which ^{238}U is converted to ^{235}U.

Compounds of Cadmium

Cadmium Oxide, CdO, is a brown powder prepared either by heating the metal so that it oxidizes, or by heating cadmium hydroxide, carbonate or nitrate, or by roasting cadmium sulphide. It does not react with aqueous solutions of caustic alkalis, but when fused with potassium or sodium hydroxide it forms cadmiates, (e.g. Na_2CdO_2).

Cadmium Sulphate, $3CdSO_4 . 8H_2O$, is prepared by the action of sulphuric acid on the oxide. This compound is used in the construction of the Weston cell, a standard of e.m.f.

Cadmium Sulphide, CdS, is sometimes called *cadmium yellow*, and finds application as a pigment; with selenium it gives the vivid red pigment, *cadmium red*.

MERCURY

Occurrence. Although a little mercury is found native in the form of globules in certain rocks, almost all the mercury of commerce is obtained from its only important ore *cinnabar*, HgS. Cinnabar is found and mined at Almaden in Southern Spain, in Tuscany in Italy, at Idria near Trieste, in California in the U.S.A., and at Nikitovka in the Donetz coal-basin of the Ukraine.

Extraction. In modern plants mercury is extracted from cinnabar by roasting the ore in retorts with lime or iron which, by combining with the sulphur, allows the liberation of the mercury. The mercury distils over and is collected in water-cooled condensers. The crude metal is then purified by distillation.

Mercury is sold on the market in strong wrought iron "flasks" containing 76 lb of mercury. The standard "flask" holding this amount of mercury is the market unit of quantity.

Physical Properties of Mercury

(*a*) At the temperature of the atmosphere mercury is a silvery-white liquid. It solidifies at $-38{\cdot}3°C$ to a solid metal which is both malleable and ductile. In the liquid state mercury is sometimes termed *quicksilver*.

(*b*) Mercury has a high density, $13{\cdot}55\ g/cm^3$ at 20°C.

(*c*) Mercury is appreciably volatile at atmospheric temperature; this volatility is increased by the presence of impurities. The vapour of mercury is very poisonous.

Chemical Properties of Mercury

(*a*) At atmospheric temperature mercury does not tarnish, but when heated in the air, or in oxygen, it is slowly oxidized, forming mercuric oxide, HgO.

(*b*) It is unaffected by water.

(*c*) Mercury reacts vigorously with the halogens to form the corresponding halides.

(*d*) Mercury is not attacked by hydrochloric acid or dilute sulphuric acid; concentrated sulphuric acid reacts with the metal to form mercuric sulphate and liberate sulphur dioxide.

Dilute nitric acid acts upon mercury very slowly, forming mercurous

nitrate and liberating oxides of nitrogen. The concentrated acid forms mercuric nitrate with oxides of nitrogen.

(*e*) The alkalis do not have an appreciable action on mercury.

(*f*) Mercury reacts with many metals to form *amalgams* often with the liberation of heat. Mercury, however does not attack metals similar to iron, and it is for this reason that mercury is often stored in wrought iron bottles. The chief metals which form amalgams include gold, silver, copper, cadmium, tin, bismuth, lead and zinc. In addition it is possible to produce what is known as *ammonium amalgam*; this latter material is prepared by placing a little sodium amalgam in an aqueous solution of ammonium chloride.

Sodium Amalgam is made by dissolving small pieces of sodium in mercury. This particular amalgam reacts with water to evolve hydrogen and forms an aqueous solution of sodium hydroxide, just as does elemental sodium. The reaction of sodium amalgam with water, however, is less vigorous than that of sodium. Sodium amalgam finds application as a reducing agent.

Zinc Amalgam is also employed as a reducing agent. Amalgams of gold and silver find application as dental fillings.

Uses of Mercury. The principal uses for mercury are in the electrical industry for mercury-arc rectifiers, for mercury switches, for automatic switchgear, for the construction of thermometers and barometers and for use in mercury boilers in which mercury vapour is used instead of steam as the working substance. It also finds use in the production of high vacua.

Other uses for mercury include its application in the manufacture of drugs and chemicals, this accounting for nearly 40 per cent of the consumption, whilst mercury fulminate used in the manufacture of blasting caps and ammunition consumes an additional 20 per cent. About 1 per cent of the consumption is in connexion with the amalgamation process for the recovery of gold.

Compounds of Mercury

Most of the compounds of mercury are probably covalent rather than electrovalent.

Mercury forms two series of compounds, mercurous compounds of the type, Hg_2Cl_2, and mercuric compounds of the type, $HgCl_2$. It is very probable that the mercury atom in the mercurous state is always part of a divalent group of two mercury atoms —Hg—Hg—.

Mercurous Compounds

Mercurous Oxide, Hg_2O, is precipitated as a black residue when sodium hydroxide solution is added to a solution of a mercurous salt—

$$Hg_2(NO_3)_2 + 2NaOH = Hg_2O \downarrow + 2NaNO_3 + H_2O$$

This oxide decomposes on exposure to light, or when heated above 100°C—

$$Hg_2O = HgO + Hg$$

Mercurous Chloride, Hg_2Cl_2 (Calomel) is made by heating a mixture of mercuric chloride and mercury when the mercurous chloride sublimes—

$$HgCl_2 + Hg = Hg_2Cl_2$$

Alternatively, calomel may be prepared by heating a mixture of mercuric sulphate, mercury and sodium chloride when the following reaction occurs—

$$HgSO_4 + 2NaCl + Hg = Hg_2Cl_2 + Na_2SO_4$$

It is also prepared in solution by the addition of a soluble chloride to a solution of a soluble mercurous salt, thus—

$$Hg_2(NO_3)_2 + 2HCl = HgCl_2 + 2HNO_3$$

Mercurous chloride is a white solid which is almost insoluble in water and in dilute acids.

It reacts with sodium or potassium hydroxide to form mercurous oxide, but with ammonium hydroxide it forms a black mixture composed of metallic mercury and white mercuric amino-chloride, $Hg(NH_2)Cl$. Solid mercurous chloride reacts with ammonia gas to form $Hg_2Cl_2 . 2NH_3$. The uses of mercurous chloride are chiefly those for medical purposes.

Mercuric Compounds

Mercuric Oxide, HgO, (Red Oxide of Mercury or Red Precipitate). Although mercuric oxide may be prepared by the heating of metallic mercury in air, this process is of a very slow nature. On a commercial scale this oxide is made by the addition of an alkaline hydroxide to the solution of a mercuric salt, thus—

$$HgCl_2 + 2NaOH \rightleftharpoons HgO\downarrow + H_2O + 2NaCl$$

If precipitation is carried out in the cold a yellow precipitate is produced, but if the solution is hot a red precipitate is produced. These differences in colour are probably due to differing degrees of fineness of the particles of the precipitate, the particle size of the yellow oxide being smaller than that of the red oxide. On heating, the yellow oxide becomes red in colour which then at 500°C changes to black. When the black material has been produced decomposition occurs into elemental mercury and gaseous oxygen. Mercuric oxide is a basic oxide which reacts with acids to form mercuric salts; it is only very slightly soluble in water, the solution having

an alkaline reaction. When acted upon by ammonium hydroxide there is formed a yellow precipitate of *Millon's base*, $2(HgO) \cdot NH_4OH$.

Mercuric Chloride, $HgCl_2$, (Corrosive Sublimate). Mercuric chloride is prepared by heating together a mixture of mercuric sulphate, sodium chloride and a little manganese dioxide. The latter is added to prevent the formation of mercurous chloride.

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4$$

The mercuric chloride sublimes as a white translucent mass. Mercuric chloride is readily soluble in hot water, but only slightly soluble in cold water; thus 100 g of water dissolve 54 g of the salt at 100°C, but only 4·3 g at 0°C. In aqueous solution, mercuric chloride is slightly hydrolysed. Mercuric chloride is readily reduced to mercurous chloride by such reducing agents as stannous chloride, thus—

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 \downarrow + SnCl_4$$

In an excess of stannous chloride, the mercurous chloride is reduced to metallic mercury, as follows—

$$Hg_2Cl_2 + SnCl_2 = 2Hg \downarrow + SnCl_4$$

Mercuric chloride is readily soluble in alcohol and in ether. Solid mercuric chloride reacts with gaseous ammonia to form the complex compound, *mercuric diammino chloride*, $Hg(NH_3)_2Cl_2$. This compound is also formed when mercuric chloride is added to a boiling solution of ammonium hydroxide and ammonium chloride. This particular compound is sometimes known as "fusible white precipitate."

If mercuric chloride is added to a boiling solution of ammonium hydroxide a bulky white precipitate of *mercuric amino chloride*, $Hg \cdot NH_2Cl$ is formed; this compound is sometimes known as "infusible white precipitate." If the first-named compound is heated it first melts (fuses) and then volatilizes, whereas the latter compound volatilizes on heating without the intermediate fusion stage.

Mercuric chloride is a strong poison. It is used for the preservation of wood, hides and fur. It also finds application in medicine and surgery.

Mercuric Iodide, HgI_2, is prepared by adding potassium iodide to a solution of mercuric chloride. An excess of potassium iodide must be avoided. Mercuric iodide is initially precipitated as a yellow solid which rapidly changes to a red colour.

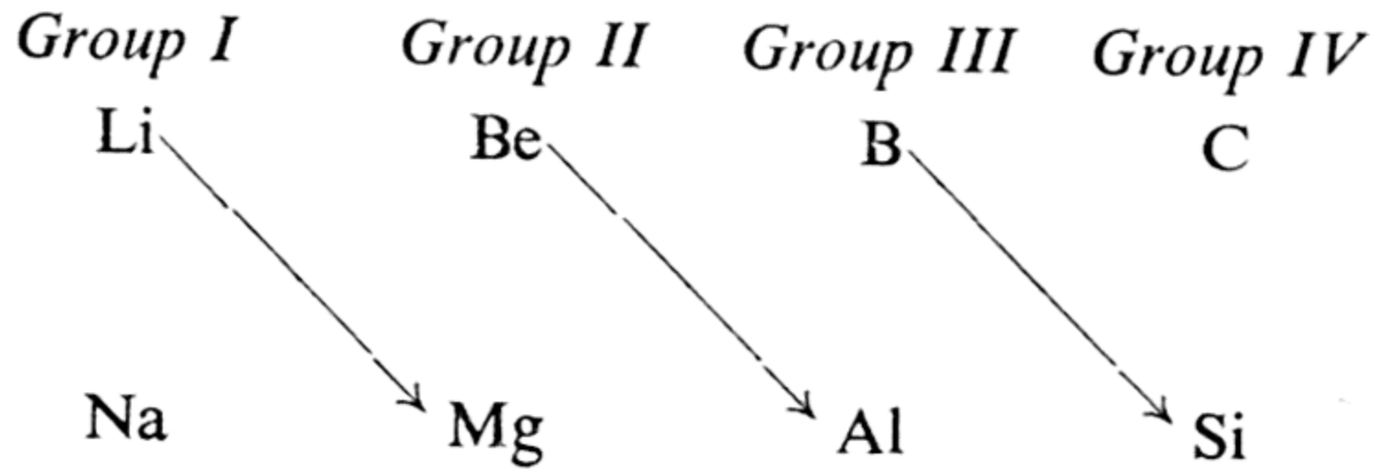
In excess of potassium iodide solution, mercuric iodide is converted into the soluble potassium mercuri-iodide, $K_2[HgI_4]$. This solution rendered alkaline by the addition of sodium hydroxide is known as *Nessler's Solution*, which is used for the detection of traces of ammonia in water (*see* p. 642).

Mercuric Sulphide, HgS, is found in nature as cinnabar. It may be prepared either by precipitation on passing hydrogen sulphide through the aqueous solution of a mercuric salt, or alternatively by the reaction of mercury, sulphur and a little potassium hydroxide solution. In the first instance a black substance results by both methods of preparation but this rapidly changes to the red sulphide. Mercuric sulphide finds considerable application as the pigment *vermilion*.

CHAPTER 21

THE ELEMENTS OF GROUP III

BORON is the first element of Group III, but its chemistry is more closely related to that of silicon, to which it is diagonally related in the Periodic Table, than to that of aluminium, the second member of Group III. This "diagonal relationship" is also found with the pairs of elements, lithium and magnesium, and beryllium and aluminium, thus—



Lithium and Magnesium. Both are silver-white metals which tarnish in air and react slowly with water. They give insoluble carbonates (and soluble bicarbonates), insoluble phosphates, and they burn in air with a similar bright light to form both oxides and nitrides. Their chlorides are very deliquescent, and their fluorides are sparingly or insoluble in water.

Beryllium and Aluminium. These elements usually occur together in nature, e.g., Beryl, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$. Their oxides are amphoteric and dissolve in both acids and alkalis; their chlorides are volatile and are readily hydrolyzed by water. So closely in fact does beryllium resemble aluminium that for a long time it was considered to be trivalent like aluminium.

Boron and Silicon. These two elements behave as typically non-metallic elements in most of their compounds. Thus their oxides are mainly acidic and dissolve in alkalis; they form oxy-acids and salts (borates and silicates), and also metallic borides and silicides. They form volatile fluorides which are similarly hydrolyzed by water; they occur together in many substances, e.g., the borosilicate glasses, and each forms a rather complex series of hydrides.

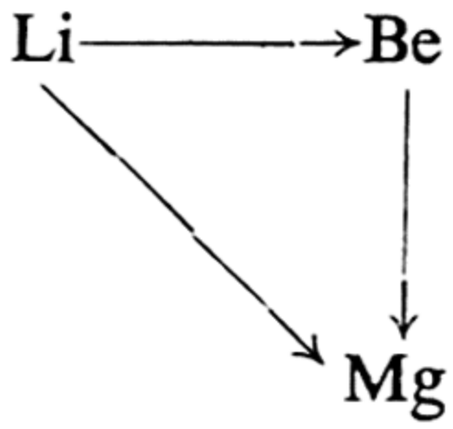
The explanation of this diagonal relationship is to be found in the effect of increasing nuclear charge on the binding of the valency electrons present in the outermost electronic orbits. If we consider the effect, for example, of changing from lithium to magnesium by way of beryllium, it is to be expected that—

(*a*) From lithium to beryllium—The increase in nuclear charge of

beryllium, compared with lithium, will result in an increased nuclear force on the valency electrons (since these may be considered to be equidistant from the nucleus).

(*b*) From beryllium to magnesium—Here the nuclear charge remains the same, but the increase in size of the magnesium atom, compared with the beryllium atom, must lead to a reduction in the nuclear force on the valency electrons (since these are now further from the nucleus).

The effects of (*a*) and (*b*) are opposed, and since they more or less cancel each other out in the total change, Li→Be→Mg, it is to be expected



that the nuclear forces on the valency electrons of lithium and magnesium should be approximately the same, and hence that these two elements should exhibit a close similarity in properties. Similar arguments also will apply to the other two pairs of diagonally related elements described above.

BORON

Occurrence. Boron does not occur free in nature, but is found in many of its compounds, such as *boric acid*, H_3BO_3, which is present in the steam jets (known as *soffioni*) which issue from the ground in the volcanic regions of Tuscany; *borax* and *tincal*, $Na_2B_4O_7 . 10H_2O$, and *colemanite*, $Ca_2B_6O_{11} . 5H_2O$, which are found principally in California and in Asia Minor. Other complex borates, such as *boracite* (Stassfürt) and *borona-trocalcite* (Chile) are also found in nature.

Extraction of Boron. The compounds and oxides of boron are not easily reduced to the element, and strong methods involving the use of other elements with a higher affinity for oxygen have to be adopted. This is exemplified by such methods as—

(*a*) By strongly heating boric oxide with magnesium (sodium, potassium or aluminium). Heating is carried out in a closed crucible to prevent atmospheric oxidation.

$$B_2O_3 + 3Mg = 3MgO + 2B$$
$$B_2O_3 + 3MgO = Mg_3(BO_3)_2$$

(*b*) By heating potassium borofluoride with potassium or magnesium.

$$3K + KBF_4 = 4KF + B$$

Boron is recovered, in the form of a dark brown powder, on boiling the resulting fused mass with dilute hydrochloric acid to remove the

potassium fluoride, magnesium borate, etc. It may be purified by heating in a vacuum at about 1200°C.

A more recent method for obtaining boron is now practised. This consists in electrolyzing a mixture of boric oxide and sodium fluoride at 1100°C. The metallic sodium liberated at the iron cathode reduces the boric oxide to boron which then deposits on the cathode. Treatment with hot hydrochloric acid gives boron as an amorphous brown powder.

A black, very hard, form of boron is prepared by strongly heating boron trichloride with hydrogen in an electric arc, and condensing the liquid boron.

$$2BCl_3 + 3H_2 = 2B + 6HCl$$

Properties. Amorphous boron, thought to be a solution of a boron sub-oxide in boron, is a dark brown powder, and is much more reactive than the black form mentioned above. It reacts rather slowly in air at about 700°C to form a superficial layer of boron oxide (B_2O_3) and boron nitride (BN), but burns at higher temperatures, and brilliantly so when heated in oxygen. Boron is one of the few elements which burns in air to form nitride as well as oxide, other elements possessing this property including lithium, magnesium, calcium and aluminium. Boron combines directly with many other elements, for example, with fluorine in the cold, and with sulphur and other halogens on heating. At higher temperatures, boron will displace carbon and silicon from their oxides

$$3SiO_2 + 4B = 2B_2O_3 + 3Si$$

Oxidizing acids, such as hot concentrated sulphuric acid and nitric acid oxidize boron to form a solution of boric acid (H_3BO_3). Boron decomposes steam at red heat, and will react with fused alkalis to form borates and liberate hydrogen—

$$2B + 2NaOH + 2H_2O = 2NaBO_2 + 3H_2$$

Uses. Boron and certain borides, such as carbon boride and silicon boride, are amongst the hardest artificial substances known, and they are likely to find increasing use as abrasives and for other wear-resistant purposes. Boron, in the form of ferroboron, added in small quantities to steel, acts as a deoxidizer, but in larger quantities (from 0·5–2 per cent boron) the boron steels, remarkable for their high strengths, are produced.

Boron, in its compounds, plays an essential part in plant life. It is known that nitrogen compounds, phosphates and potassium compounds are essential plant nutrients, but it has been shown that lack of certain other elements leads to many diseases which attack fruit and vegetable crops. Such diseases as internal cork, drought spot, rosette, and dieback in fruit trees for example are due to boron deficiency in the soil. Similarly, heart rot or dry root in sugar-beet has been traced to boron deficiency. The addition of borax to fertilizers not only prevents these diseases, but

also increases the sugar yields. Other plants affected by boron deficiency include field crops and vegetables.

Atomic Weight of Boron. Some difficulty was experienced in reconciling the atomic weight of boron obtained by applying the Dulong and Petit rule, with the smaller value to be expected from the position of boron in the Periodic Table. The latter suggested a value in the neighbourhood of eleven, and this approximate value, in conjunction with the known molecular weight of certain volatile boron compounds such as boron trichloride, established the true value of the atomic weight to be slightly less than eleven. The failure of boron to conform to the Dulong and Petit rule is due to the fact that the atomic heat of this element (beryllium and carbon also) does not reach its maximum and constant value until the temperature is considerably higher than room temperature. When the atomic heat determinations of boron are made at sufficiently high temperatures (*see* Fig. 9, p. 37) this anomalous behaviour disappears and the correct value of the atomic weight is obtained.

More accurate determinations (by Briscoe and others) have shown that the atomic weight of boron obtained from Californian sources is higher than that from European and Asiatic sources.

Source of Boron	Atomic Weight from Ratio BCl_3 : 3Ag	Atomic Weight from V.D. of BCl_3
Boric acid (Tuscany) .	10·840	10·823
Boracite (Asia Minor) .	10·819	10·818
Colemanite (California) .	10·840	10·841

These differences, although very small, are considered to be greater than the limits of experimental error, and are attributed to a slight variation in the proportion of the two isotopes of boron (at. wt. 10 and 11) although this small difference may have resulted from the different chemical treatment undergone by the boron in the three cases. This variation in atomic weight is not however peculiar to boron, as other cases are also known, particularly among the lighter elements, and these differences are all considered to be due to a very slight variation in the proportion of the various isotopes present. Thus atmospheric oxygen is perceptibly heavier than the combined oxygen present in natural waters, and potassium from plant ashes is similarly very slightly heavier than potassium recovered from marine salts.

Compounds of Boron

Boric Oxide, B_2O_3, is formed when boron burns in oxygen and also when

boric acid is strongly heated. The resulting fused mass cools to form a colourless glassy bead.

$$2H_3BO_3 = 3H_2O + B_2O_3$$

Boric oxide is the anhydride of boric acid which it forms when dissolved in water. It is almost non-volatile and so will displace other more volatile acidic oxides from their salts on strongly heating—

$$B_2O_3 + 3K_2SO_4 = 2K_3BO_3 + 3SO_3 \uparrow$$

In addition to its acidic properties, it is also very feebly basic and forms unstable salts, such as the acid sulphate $B(HSO_4)_3$ and the phosphate BPO_4. Boric oxide combines with metallic oxides on heating and also with fused alkalis to form borates, many of which possess characteristic colours (see "borax-bead test," p. 537).

$$B_2O_3 + 2NaOH = 2NaBO_2 + H_2O$$

One of the most interesting properties of boric oxide reveals itself when the oxide is used in the manufacture of borosilicate glasses. The latter have a *negative* coefficient of expansion up to about 12 per cent concentration of boric oxide, but above this value the sign changes. Boric oxide is the only substance known to behave in glasses in this way, and this property is fully exploited in the manufacture of all the modern heat-resistant glasses. It has also been found that if glass is made having a high proportion of boric oxide, then treatment with boiling dilute acids will dissolve all the boric oxide together with the soda to leave a rigid silica sponge. The latter shrinks without change of shape when it is heated to a red heat, and the resulting product is in every way similar to fused quartz. This discovery, coupled with the relative ease with which high boric oxide-glasses may be worked, has suggested a simple method for fabricating articles of quartz.

Boric Acid, H_3BO_3, is obtained commercially—

(*a*) From the volcanic steam jets ("soffioni") found in Tuscany. The boric acid solution collects in "lagoons" built around the jets, and is concentrated by the action of the steam. The boric acid then crystallizes out on cooling the concentrated solution.

(*b*) From mineral borates, such as borax, colemanite, etc., by treatment with hydrochloric or sulphuric acids. The boric acid separates on cooling, and is purified by recrystallization from hot water.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = Na_2SO_4 + 4H_3BO_3$$

Properties of Boric Acid. The purification of boric acid is based on its very slight solubility at ordinary temperatures and much greater solubility at higher temperatures—for example, 2·6 per cent at 40°C and 37 per cent at 107°C (*see* Fig. 168). It is sold commercially in various forms, such as

the colourless plates obtained by the above methods. These are soapy to the touch, a property which explains its use, for example, in the treatment of dance floors. It is also sold as the powder (boracic acid powder) and in granulated and crystal forms. It is volatile in steam, and this accounts for its presence in the "soffioni" of Tuscany.

When heated, boric acid (also known as orthoboric acid) decomposes at about 100°C to form metaboric acid, HBO_2, and at about 160°C to

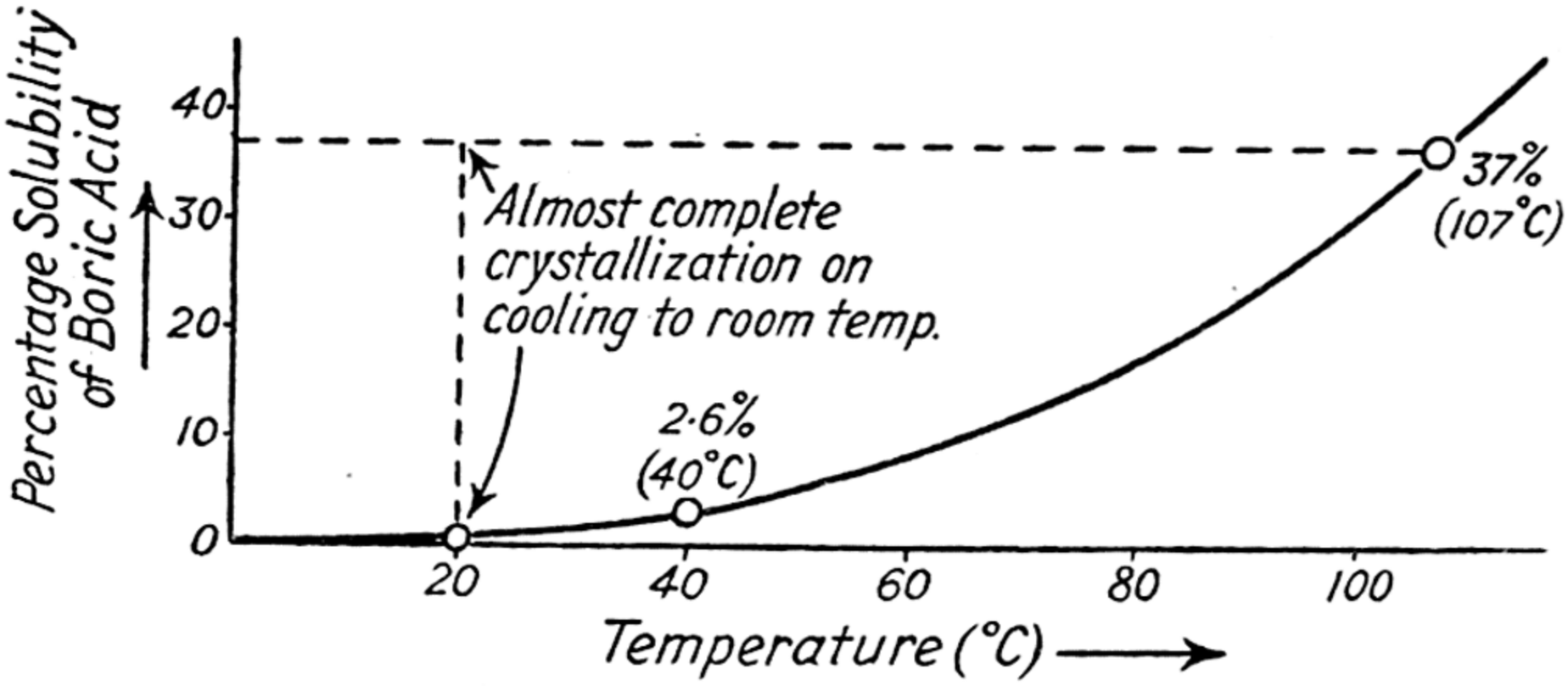


FIG. 168. Solubility Curve for Boric Acid

form tetraboric acid, $H_2B_4O_7$. At still higher temperatures, it swells and then collapses to form a glassy bead of boric oxide—

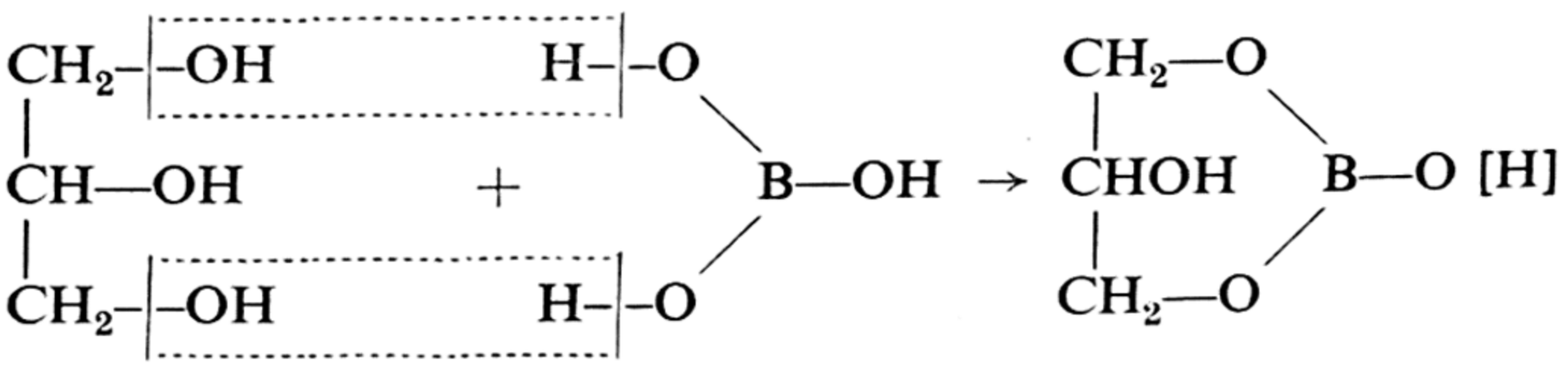
$$H_3BO_3 \xrightarrow{100°C} HBO_2 + H_2O$$

$$4HBO_2 \xrightarrow{160°C} H_2B_4O_7 + H_2O$$

$$H_2B_4O_7 \xrightarrow{> 200°C} 2B_2O_3 + H_2O$$

Boric acid is only weakly acidic, weaker in fact than carbonic acid, but its salts of the alkali-metals and most of the Group II metals are well defined. These are usually the tetra- or metaborates, the orthoborates occurring much less frequently.

Since boric acid is such a weak acid, it cannot be titrated with alkalis in the usual way. If, however, excess of glycerol be first added to the boric acid, the resulting boric-acid-glycerol complex behaves as a much stronger (although still weak) monobasic acid, and may then be titrated with standard sodium hydroxide using phenolphthalein as indicator.



$$H_3BO_3 \text{ (as complex)} + NaOH \rightarrow NaBO_2 + 2H_2O$$

Borax, $Na_2B_4O_7 . 10H_2O$. This most important boron compound is obtained commercially—

(*a*) From naturally occurring borax (and tincal), and particularly from the lower hydrate, *rasorite*, $Na_2B_4O_7 . 4H_2O$, which is found in California. From such sources, the borax is obtained pure by crystallization of the saturated solution. If the temperature of crystallization is above 60°C, the pentahydrate separates, but below this temperature, the decahydrate, $Na_2B_4O_7 . 10H_2O$, separates.

(*b*) By boiling native *colemanite* with sodium carbonate solution, and then filtering to remove the insoluble calcium carbonate and earthy matter.

$$Ca_2B_6O_{11} + 2Na_2CO_3 = 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$$

The sodium metaborate contained with the borax in the mother liquor is converted into borax by treatment with carbon dioxide gas—

$$4NaBO_2 + CO_2 = Na_2CO_3 + Na_2B_4O_7$$

(*c*) By treating boric acid with aqueous sodium hydroxide in the molecular proportions indicated by the following equation—

$$4H_3BO_3 + 2NaOH = Na_2B_4O_7 + 7H_2O$$

Properties of Borax. Since borax is the salt of a very weak acid and strong base, it is appreciably hydrolyzed by water, the solution reacting alkaline, due in effect to the reversal of the preceding equation. Since, also, methyl orange indicator is unaffected by the resulting boric acid, a solution of borax may be titrated directly against standard hydrochloric acid using this indicator. Regarding borax as $Na_2O . 2B_2O_3$, it follows, since each Na_2O will react with two molecules of HCl, that the equivalent weight of borax is equal to one-half of its molecular weight—

$$Na_2O\ (+ 2B_2O_3) + 2HCl = 2NaCl + H_2O\ (+ 2B_2O_3)$$

A normal solution will therefore contain 190·6 g $Na_2B_4O_7 . 10H_2O$ per litre.

Borax finds its most familiar laboratory use in the *borax-bead tests*. A small portion of borax is picked up on the end of a hot platinum wire, and heated in the bunsen flame. The borax first dehydrates to form a white voluminous mass, but then fuses to a clear colourless glass bead of sodium metaborate and boric oxide—

$$Na_2B_4O_7 = 2NaBO_2 + B_2O_3$$

If the bead is again fused, together with a trace of certain metallic compounds, a coloured bead is obtained, the colour of which is characteristic of the metal whose compound was used.

TABLE 87

Borax Bead Colours

Metal	Oxidizing Flame	Reducing Flame
Copper	Green (hot) Blue (cold)	Colourless or red opaque
Iron	Brown (hot) Yellow (cold)	Green
Chromium . . .	Green	Green
Manganese . . .	Violet (amethyst)	Colourless
Cobalt	Blue	Blue
Nickel	Brown	Grey or black opaque

These colours are due to the formation of coloured metaborates—

$$CuO + B_2O_3 = Cu(BO_2)_2 \quad .$$

and the different results produced in the oxidizing and reducing flames (the latter due to the reducing action of carbon) correspond, in general, to the formation of the -ous and -ic metallic metaborates, e.g. $Fe(BO_2)_2$ and $Fe_2(BO_2)_3$. In the case of the copper salts, the reducing flame may give a red opaque bead containing metallic copper—

$$2Cu(BO_2)_2 + 4NaBO_2 + 2C = 2Cu + 2Na_2B_4O_7 + 2CO$$

Sodium Metaborate, $NaBO_2 . 4H_2O$, is prepared by treating borax with the calculated amount of sodium hydroxide as indicated by the equation—

$$Na_2B_4O_7 + 2NaOH = 4NaBO_2 + H_2O$$

It is more alkaline and much more soluble in water than borax, and is used for example in "bath salts" where rapid solution is desirable.

Sodium Perborate, $NaBO_2 . H_2O_2 . 3H_2O$, is prepared either by the electrolysis of an aqueous solution of borax and sodium hydroxide or by the direct action of hydrogen peroxide on this solution.

The term *per* as applied to this compound is not strictly correct. The hydrogen peroxide is present more or less as a molecule of hydration, so that the boron atoms are not linked together through a true peroxide grouping, i.e. $>B—O—O—B<$. The commercial compound contains about 9–10 per cent of available oxygen which is liberated when the aqueous or acid solution is heated. It is nowadays used in many bleaching and other oxidation processes, and its antiseptic properties account for its increasing use in preparations such as mouth washes, tooth powders, deodorants, etc.

Uses of Borax and Boric Acid

(1) As an antiseptic in many pharmaceutical preparations, such as lotions, ointments, medicated lint and gauze, etc.

(2) Borax and boric acid play an important part in the vitreous enamelling of such articles as baths, gas and electric stoves, and enamelled kitchen ware (saucepans, etc.). The enamel used for these purposes may contain about 25 per cent of borax. The clean (sanded) article is first heated to about 900° to 950°C and the first coat of enamel applied either as a dusting powder or by a spray. The article is then returned to the furnace for a further period of about five minutes, during which time the enamel melts and forms a smooth adhering film of a borosilicate glass. Further coats are then applied up to the final white or coloured coat. The pottery industry also uses considerable quantities of borax to provide a suitably coloured glazed-surface on earthenware and china-ware. The resulting effect after the heat treatment is due to the formation of a borosilicate glaze surface.

(3) The effect of boric oxide on the expansion of glass has already been mentioned in connexion with this oxide. Considerable quantities, in the form of borax and boric acid, are consequently used in the manufacture of low-expansion, heat-resisting glasses, such as "Pyrex," used in increasing quantities in domestic kitchen ware and in laboratory apparatus.

(4) Boric acid is used in the leather industry to remove lime in the treatment of hides and skins, and borax is used to neutralize the acidity which develops in leather tanned with chromic acids.

(5) In the laundry trade, borax and boric acid are used to stiffen and impart a final gloss or glaze to the laundered article.

(6) Borax is also used as a flux in soldering and brazing, due to its reaction with, and hence removal of, metal oxides present on the surface of the metal.

Halogen Compounds

Boron Trifluoride, BF_3, a colourless fuming gas, is obtained when a mixture of boric oxide and calcium fluoride is heated with concentrated sulphuric acid—

$$CaF_2 + H_2SO_4 = CaSO_4\downarrow + 2HF$$

$$B_2O_3 + 6HF = 2BF_3\uparrow + 3H_2O$$

It reacts vigorously with water to form metaboric acid and hydrogen fluoride, the latter then combining with unchanged boron fluoride to form hydrofluoboric acid, HBF_4, reactions which recall the analogous behaviour of silicon tetrafluoride, SiF_4.

$$BF_3 + 3H_2O = HBO_2 + 3HF$$

$$BF_3 + HF = HBF_4$$

Metallic fluoborates are finding increasing use in "high-speed" and bright plating, due to their relatively high solubility and resultant rapid electro-deposition of the metal. Because of the compatibility of different metallic fluoborates with one another, it is now possible to use alloy plating baths, as for example, tin-lead fluoborate or lead-indium fluoborate baths for plating bearings and pistons with an alloy which improves their lubrication and corrosion-resistant qualities.

Boron Trichloride, BCl_3, is a colourless fuming liquid, boiling at 18·2°C, and may be prepared either by heating boron in chlorine or by strongly heating a mixture of boric oxide and carbon in a current of chlorine—

$$B_2O_3 + 3C + 3Cl_2 = 3CO + 2BCl_3$$

It fumes strongly in moist air and is immediately hydrolyzed by water—

$$\begin{matrix} Cl \\ B{-}Cl \\ Cl \end{matrix} \quad + \quad \begin{matrix} H\ OH \\ H\ OH \\ H\ OH \end{matrix} = H_3BO_3 + 3HCl$$

Boron bromide and iodide are also known.

Boron Nitride, BN, is formed when boron is heated strongly in an atmosphere of nitrogen or ammonia. Its reaction with steam to form boric acid and ammonia has been suggested as an explanation of the presence of boric acid in the *soffioni* of Tuscany.

$$BN + 3H_2O = H_3BO_3 + NH_3$$

Boron Carbide, B_4C, is prepared by heating boron oxide and carbon together in an electric furnace. It is the hardest substance so far prepared in any quantity by man, but it is not however as hard as the diamond.

$$2B_2O_3 + 7C = B_4C + 6CO$$

Boron Hydrides. When magnesium boride, Mg_3B_2 (prepared by heating magnesium and boric oxide together in a stream of hydrogen)

$$B_2O_3 + 6Mg = 3MgO + Mg_3B_2$$

is treated with a dilute acid, such as hydrochloric or better phosphoric acid, the gas evolved is mainly hydrogen, but it contains small quantities of various boron hydrides, in addition to impurities such as silicon hydrides, hydrogen sulphide, etc. The boron hydrides are isolated by passing the gas through a suitable trap cooled in liquid air, and the condensate subsequently fractionally distilled in vacuo. By this method, Stock was able to isolate small quantities of various boron hydrides, such as B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, $B_{10}H_{14}$.

Diborane, B_2H_6, however was not prepared by this method, probably

because it is rapidly decomposed by water. It has however been prepared by Burg and Schlesinger by a method involving the passing of an electric discharge through a gaseous mixture of hydrogen and boron trichloride (or tribromide) under reduced pressure. Among other things, the product contains a little B_2H_6 and rather more B_2H_5Cl. The latter is separated at low temperature, and when subsequently warmed to 0°C, decomposes to form diborane—

$$6B_2H_5Cl = 5B_2H_6 + 2BCl_3$$

Diborane is rapidly decomposed by water, and like the other boron hydrides is very reactive.

$$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$$

It should be noted that a hydride BH_3 has not so far been isolated.

Detection of Boron in its Compounds

(1) *Concentrated Sulphuric Acid and Alcohol Flame Test.* If a little borax is mixed with a little concentrated sulphuric acid, for example, in an evaporating basin, and some alcohol then added and ignited, the latter burns with a green-edged flame due to the formation of the volatile methyl- or ethyl-borate, $B(OCH_3)_3$ or $B(OC_2H_5)_3$. Copper and barium salts may give a similar green flame, however, and if these are known to be present, the test may be modified as follows.

(2) *Boron Trifluoride Test.* The borate is made into a paste with a little calcium fluoride and concentrated sulphuric acid. If the end of a platinum wire on which a little of the paste has been placed is now brought close to the edge of the base of the bunsen flame (but not in it), the volatile boron fluoride which is formed colours the flame green.

For volumetric methods for estimating boric acid and borates in solution reference should be made to these compounds earlier in the present chapter.

ALUMINIUM

Occurrence. Aluminium is the metal which is most abundant in the earth's crust, in which it occurs to the extent of 7·8 per cent as compared with 4·6 per cent for iron.

Aluminium is far too reactive to be found in the free state; it occurs in chemical combination in a wide variety of forms, the most important of which are listed on p. 542.

Extraction. Practically all the aluminium of commerce is obtained from one mineral, *bauxite*. Other minerals are used as a source of aluminium only to a small extent; these include alunite and china clay. There would appear to be little doubt that bauxite will not in the fairly near future retain its present virtual monopoly as the chief raw material for the extraction of aluminium. In what follows, however, only the extraction of aluminium from bauxite will be described.

Crude bauxite usually contains varying amounts of ferric oxide, silica, titania, and other impurities and in the first instance these must be removed otherwise the metals, iron, silicon, titanium, etc., will occur in the resulting aluminium.

Compound	Mineral and Formula
Oxide	Corundum, Al_2O_3
Hydrated oxide	Bauxite, $Al_2O_3 . 2H_2O$
	Diaspore, $Al_2O_3 . H_2O$
Aluminate	Spinel, $MgO . Al_2O_3$
Sulphate	Alunite, $K_2O . 3Al_2O_3 . 4SO_3 . 6H_2O$
Fluoride	Cryolite, $AlF_3 . 3NaF$
Silicate	Aluminium is an essential constituent of clay minerals and a large number of important silicates such as the felspars, micas, sillimanite, etc. Thus, such industrially important minerals as potter's clay, china clay, and fuller's earth are aluminium silicates

The production of aluminium on a commercial scale therefore consists of two stages, (*a*) the purification of the crude bauxite to give a pure alumina, and (*b*) the electrolysis of the purified alumina in a bath of fused cryolite containing certain other salts.

The purification of the crude bauxite is carried out in the Bayer process, the electrolysis of the alumina–cryolite bath by the Hall-Héroult process.

Bayer Process for the Purification of Crude Bauxite. In this process the essential principle involved is the treatment of the bauxite with an aqueous solution of sodium hydroxide to form sodium aluminate, from which aluminium hydroxide is precipitated, the hydroxide then being calcined to give alumina.

In practice, calcined bauxite is ground to a fine mesh and then charged into autoclaves where it is digested with an aqueous solution of sodium hydroxide for 2–8 hours under 50–70 lb pressure at 150°–170°C. The alumina of the bauxite reacts with the sodium hydroxide as follows—

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$$

The impurities ferric oxide, titania, and the greater part of the silica are unaffected by this treatment and are therefore separated as "red mud" from the filtrate containing the dissolved sodium aluminate. The sodium aluminate solution is transferred to settling tanks to which a little freshly-prepared aluminium hydroxide is added, and the whole is then stirred

(the so-called "seeding" operation) when aluminium hydroxide is precipitated from the liquor.

$$NaAlO_2 + 2H_2O = Al(OH)_3 \downarrow + NaOH$$

The aluminium hydroxide is then filtered off and calcined when a high-purity alumina is obtained.

$$Al(OH)_3 = Al_2O_3 + 3H_2O$$

Hall-Héroult Process for Electrolytic Reduction of Alumina. The furnace employed in the Hall-Héroult process consists of a rectangular box of

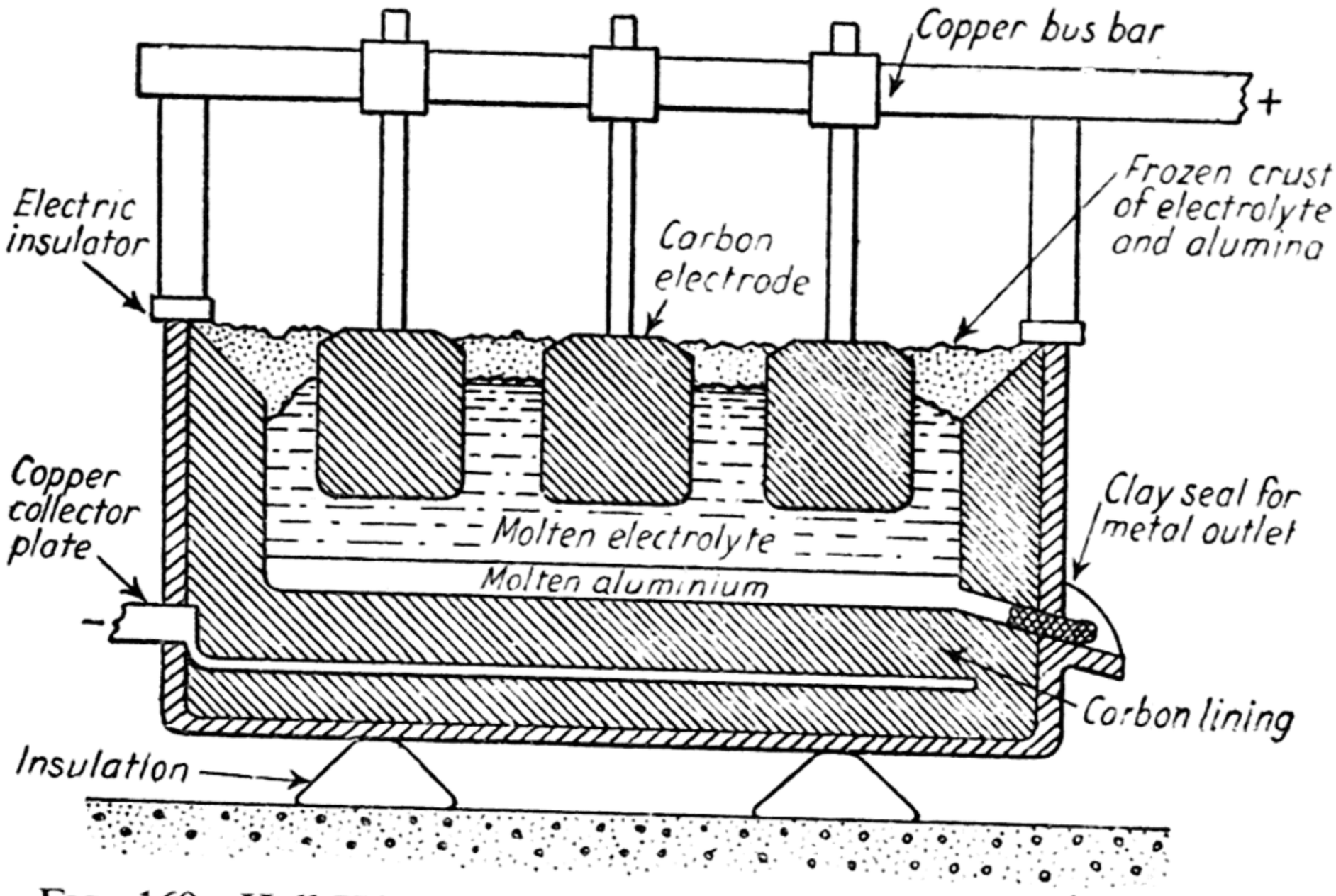


FIG. 169. Hall-Héroult Furnace for the Production of Aluminium

mild steel lined with a refractory material of low thermal and electrical conductivity; and within this a heavier lining of rammed carbon forming the cathode of the electrolytic cell (*see* Fig. 169). Plates of copper are moulded into this carbon lining to form the electrical connexion to the cathode. A typical size for this furnace casing is 8 ft long by 4 ft 6 in. wide by 2 ft high. A set of anodes is suspended in the interior of the furnace; these anodes are made of hard pure carbon. The anodes are suspended in groups of eight to twelve, clamped to a heavy frame support by suitable connexions, so that the group as a whole, or each individual anode, can be raised or lowered mechanically for the control of the current. The bottom of the furnace is inclined towards the tapping hole. When starting up a furnace, the anodes are lowered so that they make contact with a layer of granulated carbon thrown in the furnace; as the furnace heats up, cryolite

is charged in and then as this melts the anodes are progressively raised whilst more cryolite and later purified alumina as well are added. On electrolysis the aluminium collects in the molten state on the bottom of the cell from whence it is tapped off every two to three days. The density of molten aluminium is 2·29, that of the electrolyte is 2·095. The alumina content of the electrolyte ranges from 10–20 per cent. The temperature of the electrolysis is 900°–1000°C. A voltage of 5·5–7 volts is employed. Cells are connected in series of 30 to 100 and the current flowing through the cells is 8000–30 000 amp. A furnace of the dimensions quoted above produces about 120 lb of aluminium per day.

During electrolysis it is thought that the aluminium fluoride from the cryolite dissociates thus—

$$AlF_3 \rightleftharpoons Al^{+++} + 3F'$$

The aluminium ions are discharged at the cathode, whilst the fluorine ions are discharged at the anode where they react with more alumina thus—

$$2Al_2O_3 + 12F' = 4AlF_3 + 3O_2 \uparrow$$

The oxygen therefore makes its appearance at the anode where it reacts with the carbon of the anodes to form carbon monoxide which in turn burns in the atmosphere to carbon dioxide.

The purity of the aluminium produced as described above ranges from 98–99·5 per cent aluminium. Super-purity aluminium may be produced from the 98–99·5 per cent grade by electrolytic refining. In this process a copper-aluminium alloy in contact with carbon constitutes the anode of a cell, the cathode is purified molten aluminium, whilst the electrolyte is a fused mixture of cryolite, aluminium fluoride, and barium fluoride. During electrolysis the pure aluminium dissolves from the anode and is transferred to the cathode. The molten anode forms the lowest layer in the electrolytic cell whilst the molten aluminium cathode floats as the top layer; the fused cryolite mixture is sandwiched between anode and cathode. The purity of this purified aluminium is 99·8–99·9 per cent aluminium.

Physical Properties of Aluminium

(*a*) Aluminium is a silvery-white metal capable of taking a high polish.

(*b*) It is a comparatively soft metal.

(*c*) The metal has a high ductility and high malleability.

(*d*) Aluminium has a low density, 2·7 g/cm^3 at 20°C.

(*e*) It exhibits high electrical and thermal conductivities. On the basis of silver = 100, the electrical conductivity of aluminium is 62; owing to its lightness, for equal electrical conductivities, the weight of aluminium required for a conductor is about half that of copper.

(*f*) It has a fairly high melting point (657°C) and a very high boiling point (2056°C), it is practically non-volatile under ordinary circumstances.

Chemical Properties of Aluminium

(*a*) In air at ordinary temperatures aluminium is stable. When heated it oxidizes to alumina, Al_2O_3, at temperatures of the order of 700°–800°C, but the rate of reaction is slow; at still higher temperatures (950°C) it burns vigorously to form the oxide and the nitride, AlN.

(*b*) In moist air a superficial film of the oxide once formed prevents further attack on the underlying metal.

(*c*) Aluminium, on heating, combines directly with the halogens, sulphur, nitrogen and carbon to form halides, sulphide, nitride and carbide respectively.

(*d*) Aluminium reacts slowly in dilute hydrochloric acid and vigorously in the hot acid; aluminium chloride is formed and hydrogen evolved in both cases.

Dilute sulphuric acid has little action on aluminium, but the hot concentrated acid dissolves the metal, forming aluminium sulphate and liberating sulphur dioxide.

Nitric acid, both the dilute as well as the concentrated acid, reacts so slowly that it is usual to state that this acid has no action on aluminium.

(*e*) Aluminium is attacked by sodium and potassium hydroxides with the formation of the alkali metal aluminate and the liberation of hydrogen thus—

$$2Al + 2(OH)' + 2H_2O \rightarrow 2(AlO_2)' + 3H_2 \uparrow$$

The concentration of hydroxyl ions in aqueous solutions of sodium carbonate, due to hydrolysis, is sufficiently high to permit of the above reaction proceeding.

(*f*) Organic acids (e.g. acetic acid) have no appreciable action on aluminium at ordinary temperatures, but in the presence of sodium chloride they exhibit a considerable solvent effect. Likewise sodium chloride solutions corrode aluminium.

(*g*) Aluminium, being a powerful electro-positive element, is a strong reducing agent. Thus, when metallic oxides are mixed with aluminium powder and a flux and the whole ignited, the metallic oxide is reduced to metal. This is the basis of the "Goldschmidt" or "Thermit" process for the extraction of high melting point metals from their oxides. This process is of especial importance in the case of such metals as vanadium, manganese and molybdenum. This reaction is also applied to the reduction of ferric oxide to produce a small quantity of molten iron for local fusion welding, the chemical reaction in the case of ferric oxide being as follows—

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$$

It is similar for the other metals mentioned above.

Uses of Aluminium. The principal uses of metallic aluminium are for

overhead high-tension lines, for the fabrication of plant for use in the chemical, food, dairy and pharmaceutical industries, in building and for architectural purposes, in the form of foil for packaging of foodstuffs, sweets, cigarettes, etc; crumpled foil is also used for heat insulation; and in the form of powder for the manufacture of aluminium paints. Aluminium is also used as a de-oxidizer in the manufacture of steel and in the Goldschmidt process.

Aluminium-base light alloys however are of especial importance in all branches of engineering construction. In these alloys there is combined a high strength with a low density. Some of the more important of these alloys are detailed in Table 88.

TABLE 88

Compositions of Typical Aluminium-base Light Alloys

Application of Alloy	Name of Alloy	Composition (percentage by weight)								
		Cu	Zn	Mg	Mn	Si	Fe	Ti	Ni	Al
Wrought purposes	Birmabright II	3·0		1·25						Balance
	Duralumin A	4·0		0·6	0·5	0·4	0·4	0·1		Balance
	RR 77	2·25	5·0	3·0	0·5	0·4	0·4	0·2		Balance
Casting purposes	Hiduminium 23			3·0	1·25					Balance
	Alpax					13·0				Balance
	RR 53	2·0		1·6		1·0	1·3	0·1	1·2	Balance
	Y alloy	4·0		1·5		0·4	0·3		2·0	Balance

Although the strength of aluminium is raised by the addition of certain elements, the corrosion resistance of aluminium-base light alloys, particularly those containing copper, is lower than that of pure aluminium. Consequently, in order to combine the resistance to corrosion of pure aluminium with the strength of aluminium-base alloys, a composite material is in use in which sheets of aluminium alloy, such as Duralumin A quoted above, is coated on either one or both sides with high-purity aluminium; the aluminium coating is approximately five per cent of the total thickness of the sheet. Such composite material is known variously by such names as "Alclad" and "Aldural."

Anodizing

Pure aluminium owes its excellent resistance to corrosion to the presence of a hard, thin, firmly adherent and more or less impermeable skin of naturally-formed alumina. This alumina skin, which forms on contact

with the atmosphere, although soluble in alkalis and certain acids, offers strong resistance to attack by moisture and many electrolytes.

This naturally-formed alumina skin may be thickened artificially with the object of enhancing the resistance to corrosion of the material; the process employed for this purpose being known as *anodizing*. Anodizing is of particular importance in the case of aluminium-base light alloys which, as stated above, exhibit a much lower resistance to corrosion than the pure metal.

The film of thickened alumina is produced electrolytically by making the alloy the anode in an electrolyte of a 3 per cent aqueous solution of chromic acid (Bengough-Stuart process), or 15 per cent sulphuric acid (Alumilite process), or a 3–6 per cent aqueous solution of oxalic acid (Eloxal process). The metal tank—either of mild steel or lead lined—constitutes the cathode for the purpose of electrolysis. The film which is produced is very thin, normally being of the order of 0·0001 in. in thickness. The film of alumina produced on the aluminium or aluminium alloy is very absorbent immediately after its formation and it is the practice to use this property to good effect by immersing the metal article in a dyestuff, with the result that most attractive finishes are produced. Such anodized and dyed articles are used in large quantities for architectural and decorative purposes, particularly in the form of rolled and extruded sections.

Compounds of Aluminium

Aluminium Oxide, Al_2O_3 (Alumina). The occurrence of aluminium oxide in nature as corundum, bauxite and diaspore has already been discussed (*see* p. 542). On a large scale pure alumina is obtained from bauxite by the Bayer process (*see* p. 542). Alumina also occurs in nature in the form of the gem, the ruby. Synthetic rubies are now prepared on a commercial scale by the fusion of a rod of pure alumina by means of an oxy-hydrogen torch; such synthetic rubies are used for bearings in watches and scientific instruments.

In the laboratory aluminium oxide may be prepared by heating aluminium hydroxide, aluminium nitrate or ammonia alum, thus—

$$(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O = 2NH_3 \uparrow + 4H_2SO_4 + Al_2O_3 + 21H_2O$$

Properties of Aluminium Oxide. Aluminium oxide is a hard, white powder which only fuses with difficulty, its fusion point being approximately 2000°C, although it volatilizes appreciably at 1750°C.

Aluminium oxide is a very stable and unreactive substance; freshly-formed aluminium oxide however is more reactive. When heated to 900°C or above, the density of the material rises from 2·8 to 4·0 and the material becomes almost insoluble in acids.

Uses of Aluminium Oxide. Alumina is used in tremendous quantities for the extraction of aluminium as described on p. 543. But in addition to

this particular application alumina, in the form of bauxite, is used extensively for the manufacture of abrasives, high-alumina cements, and refractories. Bauxite abrasives are manufactured by fusing bauxite (or alumina) in electric furnaces; they find application in engineering under such trade names as "Alundum," "Aloxite," etc.

High-alumina refractories are employed in large quantities for the lining of high temperature furnaces (e.g. rotary kilns for calcining of cement, linings of glass melting furnaces, and high-duty boiler settings in power station plant). Some typical analyses of typical refractories are given in Table 89. From this table it will be noted that alumina is quoted

TABLE 89

Analyses of Typical Refractory Bricks

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O
Silica (steel-making) .	96·03	1·24	0·79	0·16	1·17	0·03	0·10	0·0
Silica (carbonizing) .	95·22	1·20	0·64	0·49	1·99	0·10	0·41	
Siliceous (carbonizing) .	90·16	7·75	0·46	0·57	0·22	0·16	0·35	
Siliceous fireclay . .	63·90	27·50	5·10	0·90	0·50	0·80	1·10	
Normal fireclay . .	53·60	36·80	5·70	1·10	0·70	1·00	0·90	
Aluminous fireclay .	51·28	43·14	2·06	1·88	0·48	0·28	0·68	0·28
"Sillimanite" brick .	37·72	59·19	0·62	1·65	0·21	0·03	0·41	
"Sillimanite" grog .	31·07	65·52	1·50	1·43	0·34	0·04		
Magnesite . . .	2·91	1·19	7·76		1·25	86·51		
Chromag . . .	7·00	17·00	14·00			35·00	25	
Dolomite (stable) .	12·6	2·20	3·20 (FeO)		38·6	40·9	(Cr_2O_3)	

as being present in most refractory materials; this is an important fact and it should be noted that kaolin (or kaolinite), $Al_2O_3 . 2SiO_2 . 2H_2O$, is an important constituent of all clays. Thus, alumina in the form of clay is regarded as one of the chief raw materials of the ceramic industries, sometimes known as the "clay products industries," which have as finished products a variety of articles such as chinaware, pottery, building bricks, refractories, enamels and glass. In the finished state these products are in practically all cases, essentially silicates of aluminium formed by the chemical union of alumina and silica.

Alumina, in the fused state, is also used as a refractory, but owing to its high cost its application is largely confined to laboratory uses. Aluminium oxide also finds application as an adsorption filter in the technique of analytical chemistry known as *chromatographic analysis*.

Aluminium Hydroxide, $Al(OH)_3$. Aluminium hydroxide may be prepared as a gelatinous mass when ammonium hydroxide is added to a solution of an aluminium salt.

$$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 \downarrow + 3(NH_4)_2SO_4$$

If the solution containing the suspended precipitate is heated the hydroxide becomes amorphous, and if allowed to stand in contact with dilute sodium hydroxide solution it slowly changes to the crystalline condition.

Aluminium hydroxide is amphoteric, readily reacting with acids to form salts containing the cation, Al^{+++}; and with alkalis to form aluminates containing the anion, $(AlO_2)'$, thus—

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$$

$$Al(OH)_3 + NaOH = Na(AlO_2) + 2H_2O$$

As a hydroxide, aluminium hydroxide is very feeble in its chemical reactions; thus when an aluminium salt is treated with a carbonate, carbon dioxide is liberated and aluminium hydroxide is precipitated as follows—

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Al(OH)_3 \downarrow + 3Na_2SO_4 + 3CO_2 \downarrow$$

In addition aluminium hydroxide is liberated from aluminates by such a weak acid as carbonic acid, or even by contact with its own stable form (*see* Bayer process, p. 542) in aluminate solutions.

In industry, aluminium hydroxide finds application as a mordant or dye-fixing agent in the dyeing industry and as an absorbent for the purification of sewage from colloidal and suspended matter.

Aluminium Chloride, $AlCl_3$. On a large scale, aluminium chloride is prepared by two methods, one the direct reaction of gaseous or liquid chlorine with metallic aluminium, thus—

$$2Al + 3Cl_2 = 2AlCl_3$$

the other method consisting of the simultaneous reduction by carbon and chlorination by gaseous chlorine of alumina-bearing materials such as bauxite, thus—

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO \uparrow$$

In the first process the reaction is sufficiently exothermic to vaporize the aluminium chloride as it is formed; the reaction between alumina, carbon and chlorine is, however, endothermic, and heat therefore must be supplied to cause the reaction to proceed. In this latter process briquettes of bauxite and carbon are charged into a shaft kiln where the combustion of the carbon in a blast of air provides the necessary heat. Chlorine is also blown into the kiln, when the aluminium chloride is volatilized and condensed.

In the laboratory the action of hydrochloric acid on metallic aluminium produces a solution of aluminium chloride from which on evaporation crystals of the hexahydrate, $AlCl_3 . 6H_2O$, may be obtained. The anhydrous salt may be obtained by heating crystals of the hydrate in an atmosphere of hydrogen chloride or of chlorine.

Properties of Aluminium Chloride

(*a*) Anhydrous aluminium chloride is a white, crystalline substance.

(*b*) It is extremely deliquescent; in moist air fumes are produced because of the formation of hydrogen chloride as follows—

$$AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl \uparrow$$

(*c*) On heating, aluminium chloride vaporizes readily at 183°C, without melting. At temperatures between 183° and 400°C, the vapour consists of Al_2Cl_6, but at 400°C, dissociation to $AlCl_3$ commences and is complete at about 750°C.

(*d*) Aluminium chloride dissolves freely in water, the solution exhibiting an acidic reaction because of hydrolysis.

Uses. Aluminium chloride finds considerable application in the chemical industry as a catalyst in many organic chemistry reactions, and in the petroleum industries.

Aluminium Sulphate, $Al_2(SO_4)_3$. On a laboratory scale, aluminium sulphate is prepared by the action of sulphuric acid on the metal or aluminium hydroxide. On evaporation of the resulting solution crystals of $Al_2(SO_4)_3 \cdot 18H_2O$ are obtained.

On a commercial scale aluminium sulphate is made by the action of sulphuric acid upon bauxite or upon china clay. The reactions involved are as follows—

(i) $$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O$$

(ii) $$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 3H_2SO_4 = Al_2(SO_4)_3 + 2SiO_2 \downarrow + 5H_2O$$

The crude aluminium sulphate is known as *alumina–ferric*. Aluminium sulphate is used for the purification of water for domestic purposes. In such water, particles of fairly large dimensions can be removed by sand filtration but finely divided and colloidal impurities must first be coagulated before they can be removed by filtration. It is in this connexion that aluminium sulphate is employed. When aluminium sulphate is added to neutral waters it suffers hydrolysis as follows—

$$Al_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Al(OH)_3 \downarrow + 3H_2SO_4$$

In order to render the aluminium hydroxide filterable it is necessary to destroy the sulphuric acid formed—this is done by the addition of alkali; the reaction given above then proceeds to completion.

Aluminium sulphate is often used in conjunction with sodium aluminate, thus—

$$Al_2(SO_4)_3 + 6NaAlO_2 + 12H_2O = 8Al(OH)_3 \downarrow + 3Na_2SO_4$$

The precipitated aluminium hydroxide traps the colloidal impurities in water undergoing treatment by simple entanglement as well as by

adsorption of the colloid, with the result that the aluminium hydroxide is then in a form which is readily filterable.

Other uses for aluminium sulphate include its application to the dyeing industry when it is used as a mordant, as a filler in the manufacture of paper, and in the tanning of leather and the waterproofing of cloth.

Alums

When a solution containing dissolved potassium sulphate and aluminium sulphate is evaporated, colourless crystals of the double sulphate of potassium and aluminium are obtained, having the formula—

$$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$$

This substance is known by the name of *alum* or more specifically as *potash alum*. This compound is used as a mordant. Potash alum is a typical member of a group of compounds known as the alums which have the general formula $M_2(SO_4) . N_2(SO_4)_3 . 24H_2O$, where M represents an atom of a univalent metal such as potassium, sodium, lithium, rubidium, caesium, silver, univalent thallium, or the ammonium radical, and N represents an atom of a trivalent metal such as aluminium, chromium, iron (ferric), manganese, cobalt, or gallium.

Thus, there are capable of preparation a whole range of alums of which the following are typical members, in addition to potash alum described above. All the alums crystallize in the form of octahedral crystals.

Ammonia Alum, $(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ is a colourless compound which on ignition leaves a residue of alumina.

Ferric Alum, $(NH_4)_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$ is a pale-violet coloured compound.

Chrome Alum, $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$ crystallizes in the form of dark purple crystals. This alum may readily be prepared by the reduction of potassium dichromate with sulphur dioxide as follows—

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

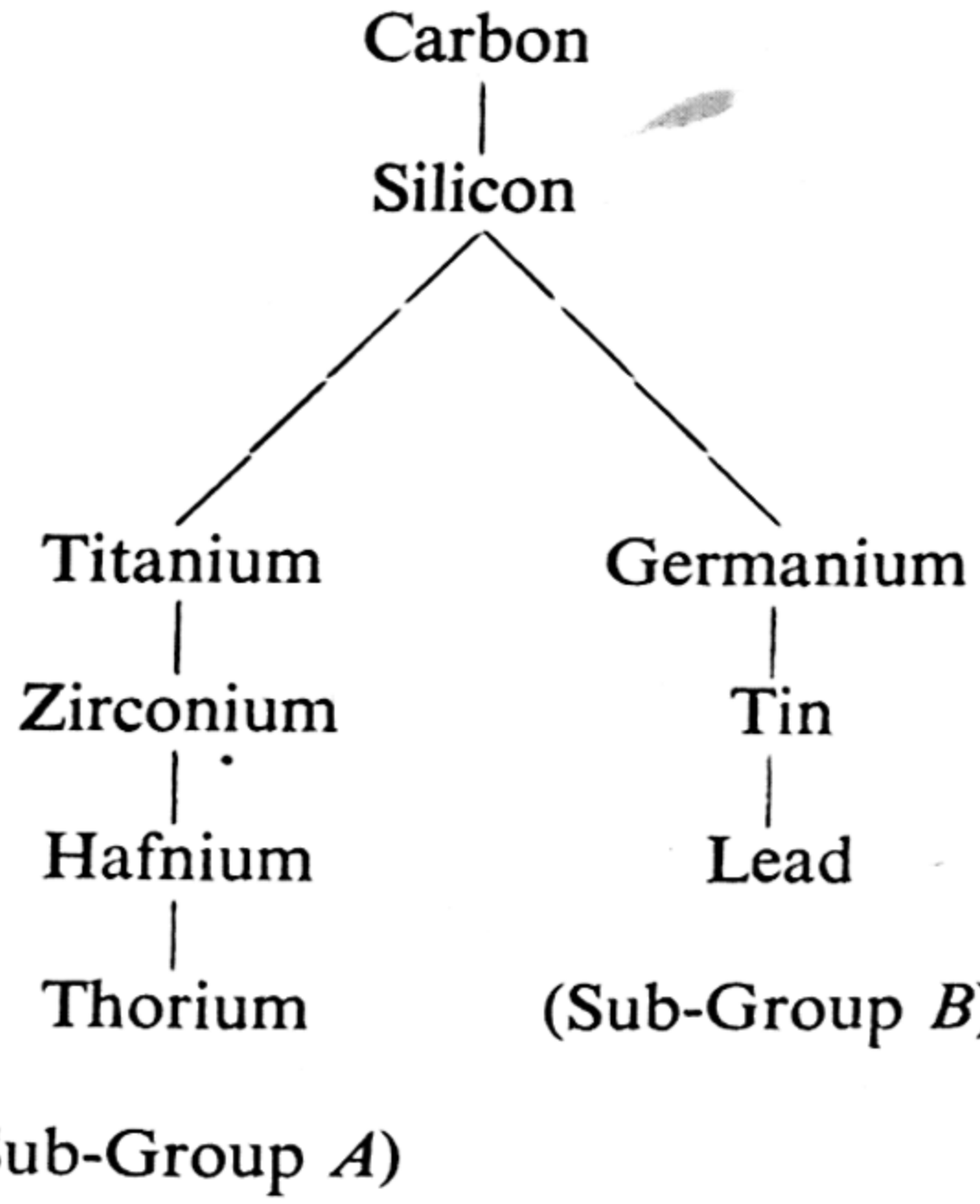
On evaporation of the solution containing equimolecular proportions of potassium sulphate and chromium sulphate, chrome alum separates out. All the alums are isomorphous with one another.

There is also a series of *selenium alums* in which a selenium atom substitutes for the sulphur atom present in potassium sulphate.

CHAPTER 22

THE ELEMENTS OF GROUP IV

In the accompanying chart the elements of Group IV are arranged in their order of increasing atomic weights. The first two, carbon and silicon, are typically non-metallic but the remaining elements show increasing metallic character with increasing atomic weight.



The normal valency of the Group IV elements is four, but lower valencies (principally two) also occur with the heavier elements. In the four-valency state, the resulting compounds are all covalent (recent work, however, suggests that the plumbic ion, Pb^{++++} may exist) and this covalent nature is reflected in the volatile nature, absence of salt-like properties and ease of hydrolysis of the tetra-halides ($SiCl_4$, $TiCl_4$, $SnCl_4$, $PbCl_4$, etc.). Carbon tetrachloride is exceptional in the latter respect in that it is not hydrolyzed by water; the reasons for this difference, however, are discussed on p. 555.

There is the same tendency as in other Groups of the Periodic Table for the elements with the higher atomic weights to occur also in lower valency states. Thus tin and lead in particular show a stable *electro-valency* of two in their stannous and plumbous salts (for example, stannous chloride, $SnCl_2$, and plumbous chloride or lead chloride, $PbCl_2$, etc.). This stable divalency is explained by the "inert character" of the first two electrons of the outermost quantum group. These two electrons, which

from a complete sub-quantum group, are often referred to as the *inert-pair*, shown in brackets below.

Sn	2	.	8	.	18	.	18	. 4
Sn^{++}	2	.	8	.	18	.	18	. (2)

The univalency of thallium (Group III) in many of its compounds and the trivalency of bismuth (Group V) are similarly explained in terms of the inert-pair.

CARBON AND SILICON

The chemistry of these elements is remarkable for the very large number of stable compounds in which they occur in nature. The rock, soil and sand of the earth's crust are composed predominantly of silicon compounds, whilst the vegetation and life which abound on its surface are almost entirely composed of various carbon compounds.

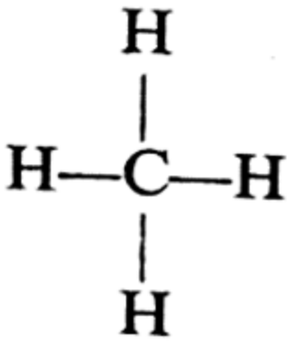
Carbon, for example, occurs in the celluloses, sugars, fats, oils, etc., and the association of these compounds with life in its various forms led to the term *organic* being applied to the compounds of carbon. Nowadays, it is recognized that although many of these compounds result from living processes they may also be produced by the ordinary chemical reactions associated with inorganic chemistry. The term *organic chemistry* is still retained, however, but this term now implies the chemistry of carbon compounds, irrespective of whether such compounds occur naturally or are produced in the laboratory.

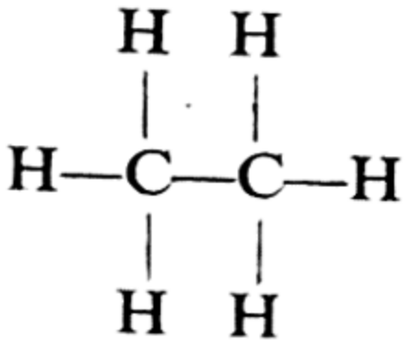
The existence of so many carbon compounds (several hundred thousand are already known) is due to—

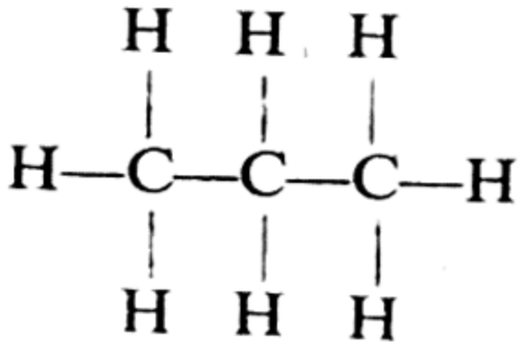
(*a*) The ability of carbon to form stable covalency bonds with other non-metals (hydrogen, oxygen, halogens, etc.) and particularly so with itself without any fundamental change occurring in the properties of the resulting compounds. For example, CH_4, C_2H_6, CCl_4, CS_2, etc., have many properties in common.

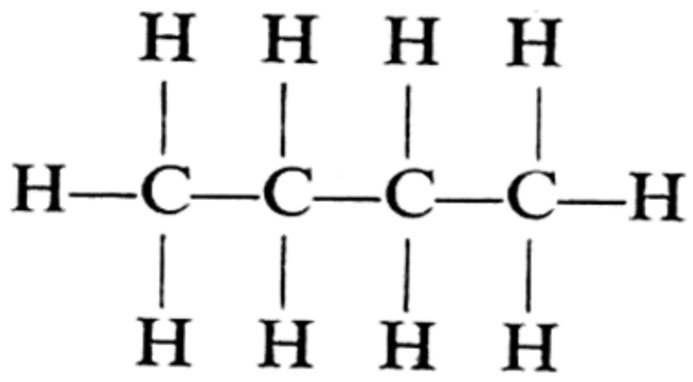
(*b*) The valency of carbon is uniformly four. Other non-metals show not only different numerical valencies towards hydrogen on the one hand and towards the halogens on the other, but the resulting compounds are often quite different in their chemical properties (e.g. H_2S and SF_6; PH_3 and PCl_5, etc.).

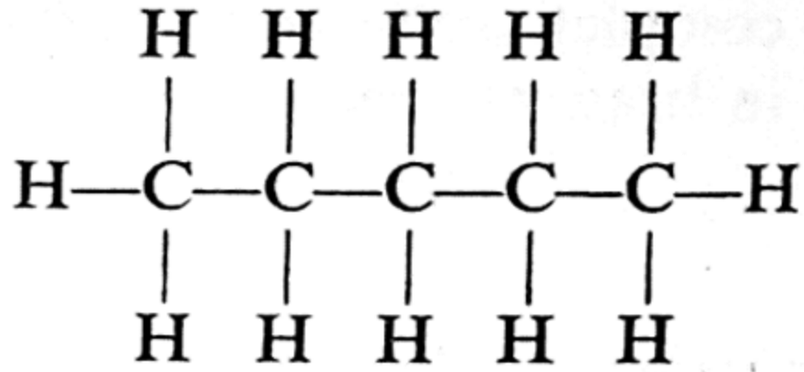
(*c*) The ability of carbon to form compounds based on an apparently unlimited number of co-linked carbon atoms. The following examples from the paraffin (hydrocarbon) series are typical of the many homologous series which occur in organic chemistry—







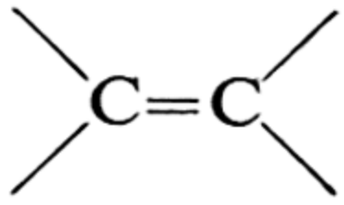




Carbon differs from silicon in the following important respects—

(i) The —Si—Si— chain decreases in stability with increase in the number of silicon atoms involved. This effectively limits the number of silicon compounds based on this —Si—Si— framework to the simpler members, such as SiH_4, Si_2H_6, Si_3H_8, etc.

(ii) Silicon does not form unsaturated compounds containing double and triple bonds, such as occur in many organic compounds—

e.g. Ethylene  Acetylene —C≡C—, etc.

(iii) Whereas carbon dioxide is a gas with the simple molecular structure O=C=O, silicon dioxide (*silica*) is a solid with a very high melting point (> 2000°C), and has a so-called "giant-molecule" structure based on a three dimensional net-work of alternate silicon and oxygen atoms, as shown (in two dimensional perspective) in the following diagram—

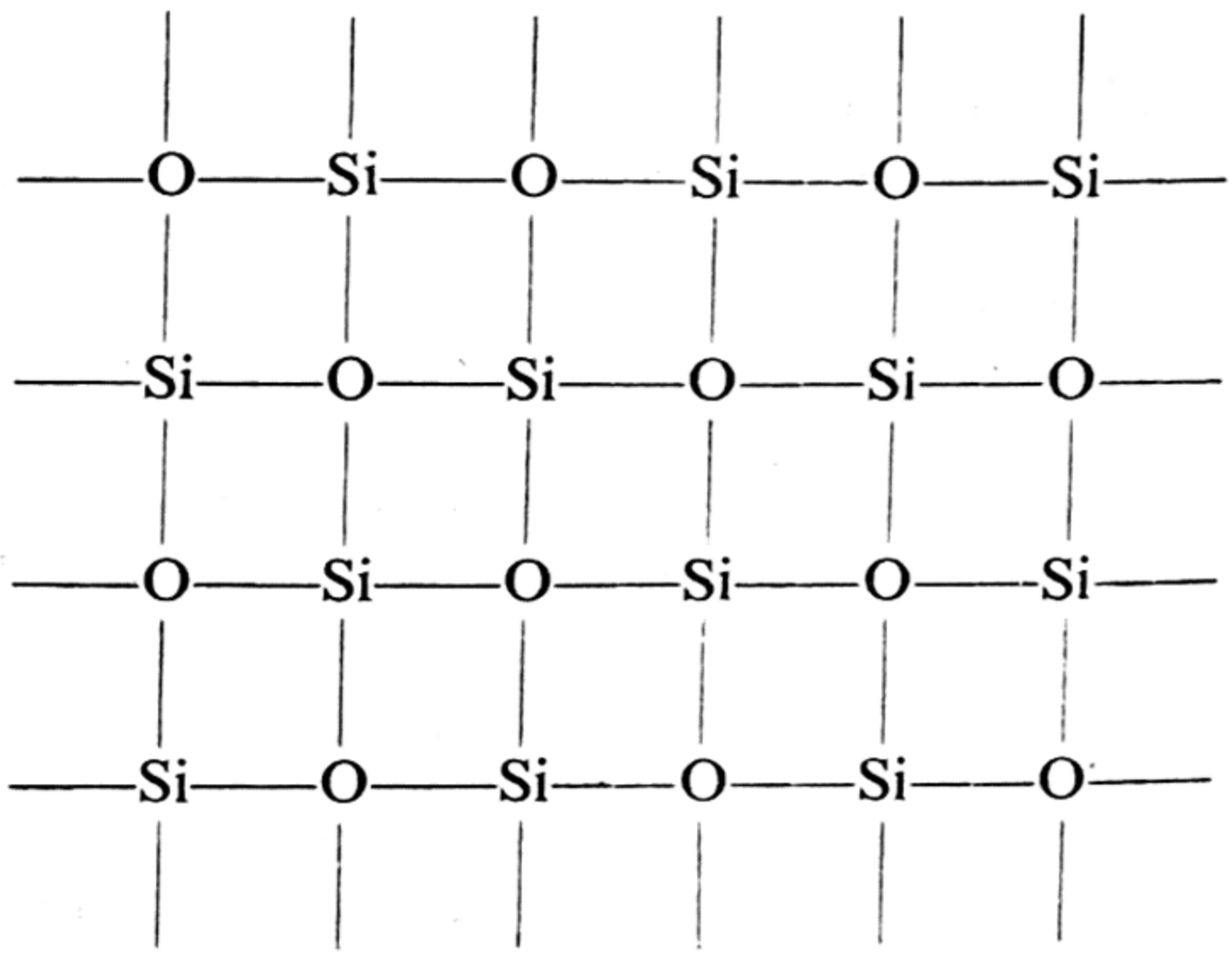


FIG. 170. Silica Structure in Two Dimensional Perspective

Silicon does not form double covalent bonds with oxygen, but instead forms very stable single bonds, without limit apparently to the numbers of silicon and oxygen atoms so united. The linkage —Si—O—, in fact, appears to play as fundamental a role in the chemistry of the large number of silicate compounds which make up the earth's crust as the —C—C—

linkage plays in the chemistry of the even larger number of organic compounds which result from living processes on the earth's surface.

(iv) The existence of such compounds as H_2SiF_6 and $SiF_4(NH_3)_2$ shows that silicon is not completely saturated in its four-covalency state. The reactions—

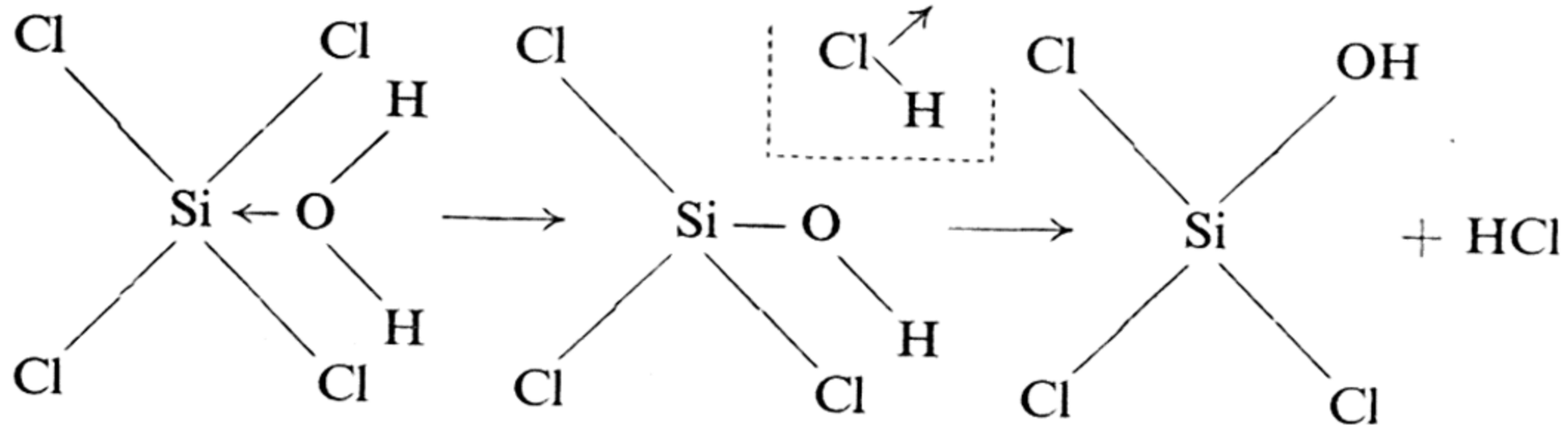
$$2HF + SiF_4 = H_2[SiF_6]$$

and

$$2NH_3 + SiF_4 = H_3N \rightarrow Si \leftarrow NH_3$$

(F atoms above and below Si)

are essentially addition reactions in which silicon reveals its higher co-ordination number of six as compared with the maximum of four for carbon. This ability of silicon to co-ordinate additional atoms or molecules, a property possessed also by the other Group IV elements, but not by carbon, explains why carbon tetrachloride alone of the Group IV halides is not hydrolyzed by water. Considering the hydrolysis of silicon tetrachloride, the first reaction presumably is to co-ordinate a molecule of water, followed by the elimination of a molecule of hydrogen chloride, thus—



The net result is to replace chlorine by hydroxyl. This process repeated four times ultimately results in the substitution of each halogen atom by a hydroxyl group, as expressed in the equation—

$$SiCl_4 + 4H_2O = \underset{\text{silicic acid}}{Si(OH)_4} + 4HCl$$

Carbon tetrachloride cannot form such intermediate addition compounds with water and so is not hydrolyzed.

THE CARBON CYCLE IN NATURE

Carbon occurs in the free state in nature as diamond, graphite and in a less pure form in coal. Its compounds occur extensively in nature and are essential constituents of all forms of plant and animal life. These substances, whether free or in the combined state, owe their existence in

the first instance to the presence of carbon dioxide in the atmosphere. The green colouring matter, chlorophyll, present in the leaves and stems of plants, enables the latter to utilize solar energy to convert this carbon dioxide into various sugars by the following photosynthesis—

$$6CO_2 + 6H_2O + 660\,000 \text{ cal.} = C_6H_{12}O_6 + 6O_2$$

Some of the sugar is used by the plant as food sugar (during which it is converted back to carbon dioxide and water with the liberation of heat energy). The remainder is converted by the plant into starch and cellulose, which form the principal solid constituents of all vegetable tissue, and the foodstuff for herbivorous animals. Carnivorous animals, in their turn, obtain their carbon foodstuffs from the flesh of other animals. The slow combustion of these carbon compounds, which provides the energy necessary for the existence of all forms of plant and animal life, is essentially a reversal of the above photo-synthesis. Oxygen provided by the atmosphere is thereby converted into carbon dioxide gas which is returned to the atmosphere. The carbon cycle is then complete; it provides the means whereby solar energy is stored so that it may later be utilized to sustain all forms of life.

Coal is produced by the accumulation of vegetable matter throughout the ages. By bacterial oxidation and other processes some carbon, hydrogen, oxygen, and heat energy are lost, and the vegetable matter is slowly converted into peat, lignite and other coals of increasing hardness and carbon content. In effect, the original solar energy absorbed by the plant is concentrated and preserved as solid fuels. This energy may however be released at any stage of the process by burning the fuel in an adequate supply of oxygen when, as before, carbon dioxide is formed and returned to the atmosphere. These natural fuels thus act as a storehouse of solar energy which is released by the completion of the carbon cycle.

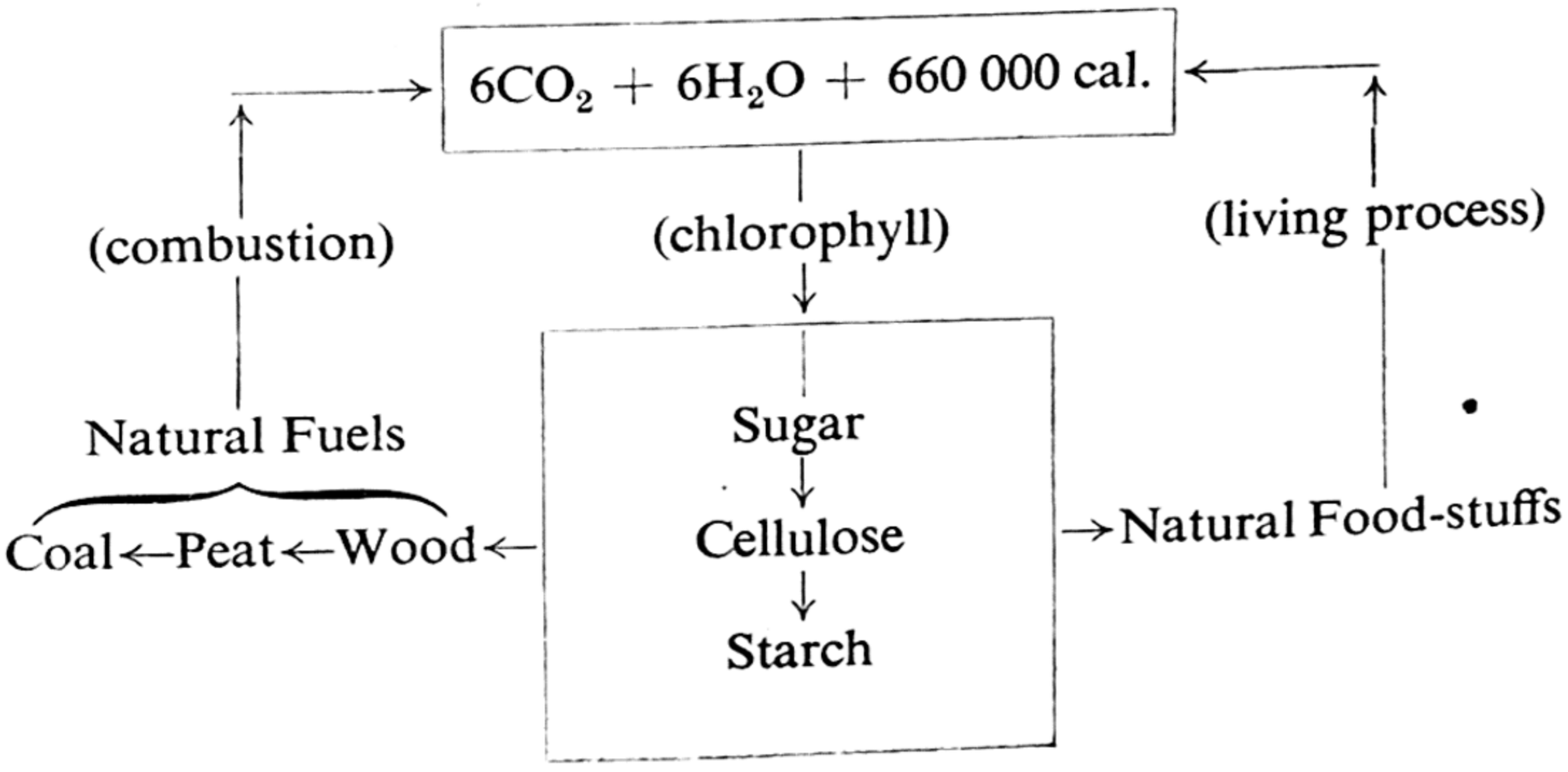


FIG. 171. The Carbon Cycle

Allotropy of Carbon

There are two different crystalline allotropic forms of carbon and both occur in nature. These are the diamond and graphite. Both have been examined by the methods of X-ray crystal-structure analysis.

Diamond consists of a regular three-dimensional array of carbon atoms in which each carbon atom is linked tetrahedrally and covalently to the next carbon atom.

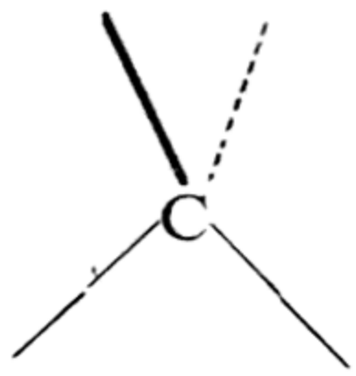


FIG. 172. Tetrahedral Arrangement of Carbon Valency Bonds

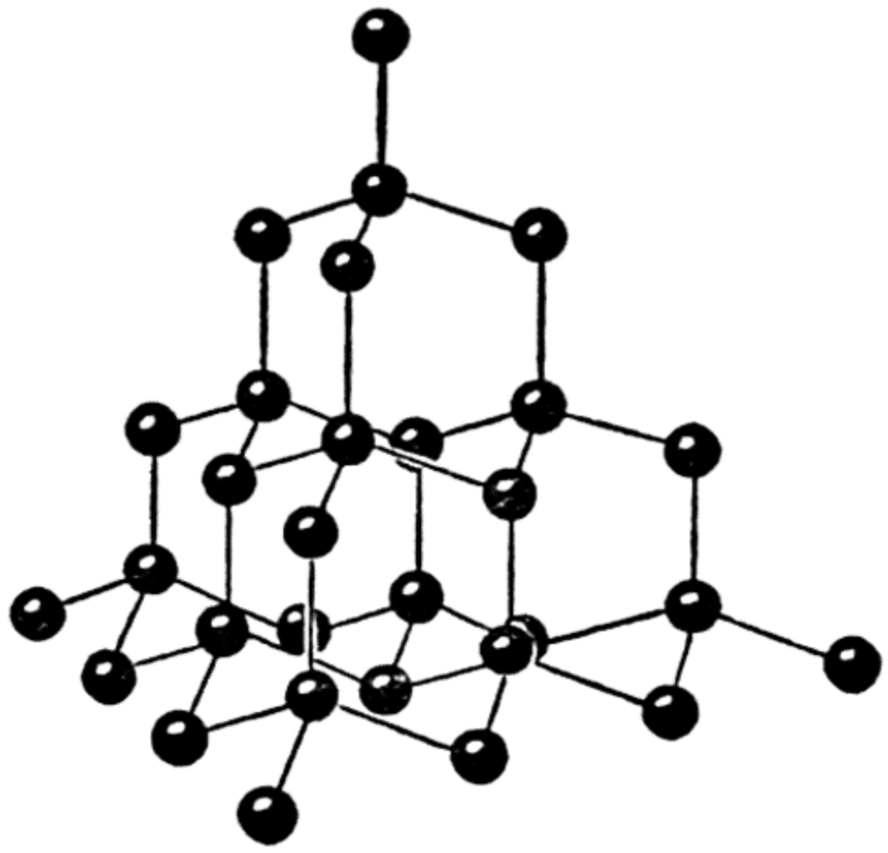


FIG. 173. Portion of Diamond Structure

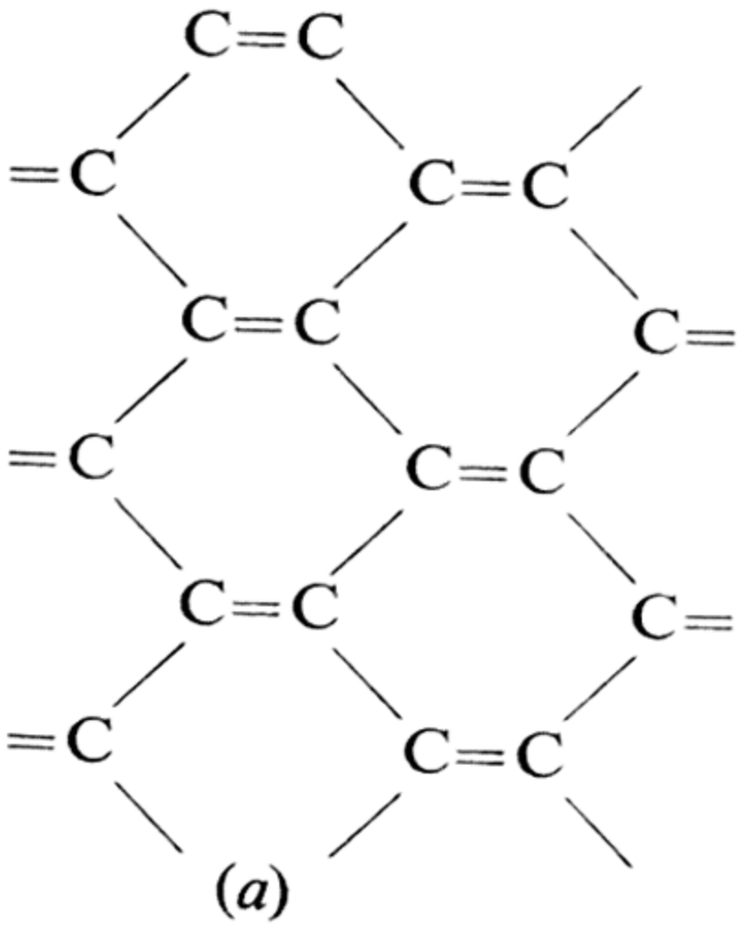


FIG. 174. Graphite Structure: Hexagonal Arrangement of Carbon Atoms

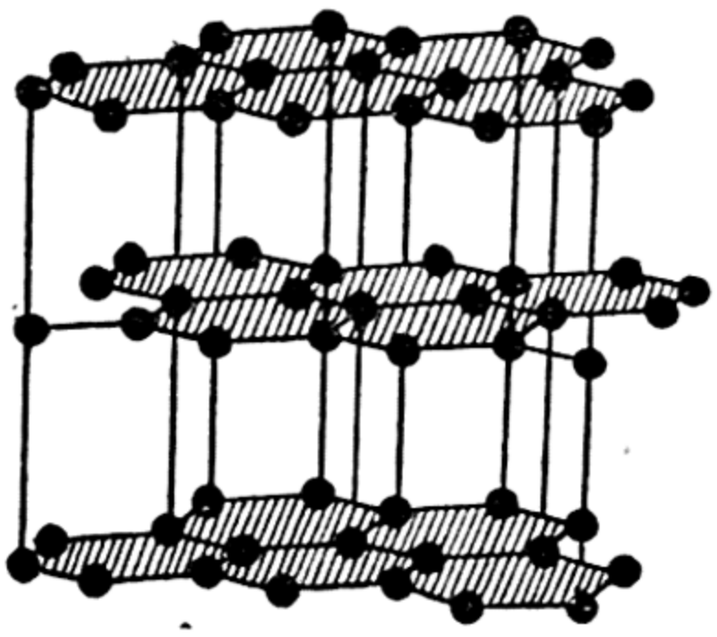


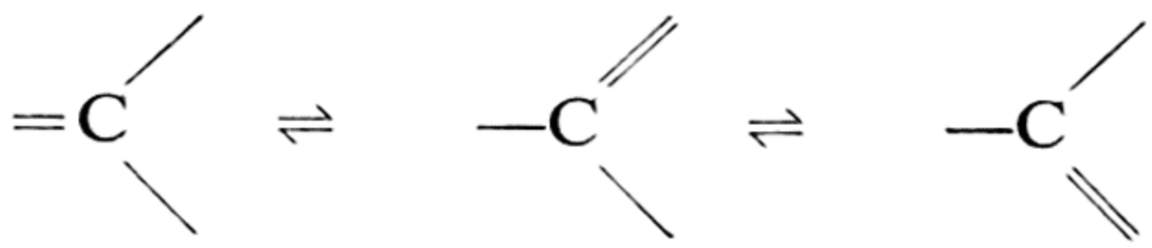
FIG. 175. The Arrangement of Planes of Carbon Atoms in Graphite

This arrangement of the carbon atoms to form a giant-molecule explains the important physical properties of diamond, such as its very great hardness and the very high temperature at which it volatilizes. The former property follows from the rigid nature of the lattice and the absence of any planes of weakness in the crystal structure, whilst the latter property results from the absence of simple molecules held together by relatively weak van der Waal's forces, such as occur in most molecular crystals of low melting point (e.g. organic compounds). The diamond consequently does not melt, but at very high temperatures (3600°C approx.) the increased

vibrational energy content results in the splitting off of carbon atoms so that diamond vaporizes.

Graphite, on the other hand, has a two-dimensional sheet-like structure. Each layer is composed of covalently-linked carbon atoms which form a hexagonal-ring network. These layers are arranged parallel to other similar layers to which they are united not by valency bonds but rather by much weaker electrostatic forces of the van der Waal's type.

The C—C distance in each plane is 1·42 Å units. Since the C—C single-bond distance (found for example in diamond) is 1·54 Å units, and the C=C double-bond distance (for example, in ethylene) is 1·34 Å units, this intermediate value of 1·42 Å units suggests that each plane of carbon atoms in graphite is a resonance hybrid of structure as shown in Fig. 173 and of the other two structures having the alternative arrangement of the double and single bonds. Such resonance would then give each C—C bond one-third double bond character, i.e.—



The relatively large distance apart of these carbon sheets (3·4 Å units) suggests that they are held together only by weak Van der Waal's forces. This weakness enables the sheets to slide relatively and parallel to each other with only a minimum of effort, a behaviour which likens graphite to a pack of playing cards, and also explains its excellent lubricating properties.

The so-called amorphous forms of carbon (charcoal, lampblack, coke, etc.) are all graphitic in character. They are composed of portions of the graphite structure and are most simply described as a random aggregate of microcrystals of graphite.

Recent investigations, however, suggest the existence of a third crystalline form of carbon in certain amorphous carbons. This form has a structure which is related to the graphite structure, but is very much more highly porous due to a three-dimensional cross-linking of the hexagon rings present in graphite. This third form of carbon in fact appears to have an open three-dimensional structure not unlike the "skeleton-structure" of some zeolites (*see* p. 605). Such a structure would explain the exceptionally high adsorptive power of certain activated carbons and in particular of the amorphous carbons producted by carbonizing (heating) calcium mellitate or by treating hexachlorobenzene, C_6Cl_6, with sodium.

Diamond occurs rather sparsely in various parts of the world, such as South Africa, Brazil, the Ural Mountains, Australia, and elsewhere. The principal source is South Africa where the diamonds occur in a type of rock known as "blue ground," which is found in cone-shaped depressions, or "pipes," thought to be the necks of extinct volcanoes. This

rock is mined and then exposed to the weather when it slowly crumbles to a powder from which the diamonds are recovered by handpicking or washing methods. At this stage the diamond appears in the form of a rounded pebble which has to be cut and polished by highly skilled craftsmen before it emerges as the brilliant sparkling gem-stone.

The most valuable varieties of diamond are those which are clearest and least coloured. These are referred to as "diamonds of the first water." Other less valuable diamonds are coloured yellow, red, green, pink, and even blue, due to the presence of metallic impurities. The least valuable are those which are more deeply tinted grey or black. These are known as "carbonado" or "boart," and although lacking in value as gem-stones, the fact that they are still diamonds, and therefore very hard, makes them especially valuable as abrasives in the cutting and polishing of other gem-stones (including the diamond), for the cutting edges of most present-day high-speed metal-turning machinery and for the tips of rock-drilling plant. They are usually referred to in this connexion as industrial diamonds.

The two physical properties of diamond which stand out above all others are its abnormally high refractive index and its very great hardness. In its final cut and polished form as a gem-stone it is provided with a geometrical arrangement of artificial faces or facets so as to take the maximum advantage of its very high index of refraction (2·4) and dispersive power. The rainbow or spectrum of primary colours which is produced for example when ordinary white light is passed through a glass prism gives a simple picture of the effect produced on a more elaborate scale by the cut diamond. Of greater importance industrially is the fact that the diamond is the hardest of all substances. (The hardest substances so far produced on any significant scale by man are boron carbide and crystalline boron.) Reference to the crystal structure of diamond, a portion of which is shown on p. 557, shows that this very great hardness results from the unique way in which the carbon atoms are linked together in a uniform solid three-dimensional structure to form one giant-molecule.

Other physical properties of diamond include its specific gravity (3·5, cf. 2·25 for graphite), and owing to its crystalline nature, its ability to transmit X-rays. Imitation diamonds made of glass, a non-crystalline material, are opaque to X-rays. This difference offers a simple means for distinguishing between real and artificial diamonds.

Diamond is not very active chemically. It burns in air with difficulty at 900°C, or in oxygen at about 700°C, to form carbon dioxide; it is not attacked by acids nor by alkalis, but may be oxidized to carbon dioxide by treatment with a mixture of potassium dichromate and concentrated sulphuric acid at about 200°C. Reaction occurs with fluorine at about 700°C to form carbon tetrafluoride, CF_4.

That diamond is an allotrope of carbon may be shown by determining the weight of carbon dioxide produced by the complete combustion of a

weighed amount of diamond. The experiment may be carried out by strongly heating the diamond in a current of oxygen and absorbing the carbon dioxide in weighed potash bulbs provided with a phosphorus pentoxide moisture trap.

Very little success has attended man's efforts to synthesize diamonds. The largest synthetic diamond was produced in 1936 by Hershey at McPherson College, and measured $2 \times 1 \times 1$ mm. The earliest evidence that diamonds could be prepared by crystallization at very high temperatures and pressures was obtained from the successful experiments of Moissan, who heated pure iron with sugar charcoal in a carbon crucible in an electric-arc furnace. The molten iron, so produced, dissolved the carbon, and when the temperature reached about 4000°C this solution was rapidly cooled by plunging the crucible into molten lead (m. p. 327°C). This sudden cooling first solidifies the outer layer of cast iron. As the interior cools and the iron solidifies from the surface inwards, the carbon is so to speak pushed to the centre where the cast iron is last to solidify, and there crystallizes out under enormous pressure (since cast iron expands on solidification). When the iron was subsequently dissolved away by treatment with acid, some graphite, some boart and a few very small diamonds were recovered.

Graphite, the other pure crystalline allotrope of carbon, occurs more abundantly in nature than does the diamond. The major deposits are found in Korea, Ceylon, Madagascar, Mexico, and in Germany (although extensive deposits formerly occurred in this country at Borrowdale in Cumberland), and are usually associated with impurities such as quartz, calcite, and silicate minerals. The graphite usually requires concentration, for example, by hand-picking or by more modern methods involving flotation, electrostatic and electromagnetic separation. Some graphites swell when moistened with nitric acid and this enables them to float away more easily from the gangue. Other chemical processes include treatment with hydrochloric acid, caustic soda, and also with hot water, as a result of which the graphite becomes more plastic and may then more easily be pressed into blocks, plates, rods, etc.

In the trade, the name *graphite* is reserved for the crystalline flake mineral; the massive variety is termed *plumbago* and the more finely divided amorphous form, used in stove polishes, pencils, etc., is known as *black lead.* They are, however, all different physical forms of the same allotrope, graphite.

Graphite is also manufactured artificially (at Niagara) from amorphous carbon by the Acheson Process. A mixture of petroleum coke and sand, together with a little binding material such as coal-tar, is packed into a rectangular fire-brick furnace provided with heavy carbon electrodes as shown in the diagram on p. 561.

A central core of carbon-rods between the two electrodes conducts the

current through the charge, which is raised to and maintained at a very high temperature for some twenty-four to thirty hours. At the end of this period, the furnace is dismantled and the graphite collected. The reactions which occur are expressed in the following equations—

$$SiO_2 + 5C = 3SiC + 2CO$$

$$SiC = Si + C$$

graphite

The silicon carbide (carborundum), first produced, decomposes at the very high temperature involved, the silicon distilling off and the carbon remaining as graphite.

Graphite is an opaque, flaky crystalline solid with a characteristic greasy feel and a slightly metallic grey lustre. Its more open crystalline

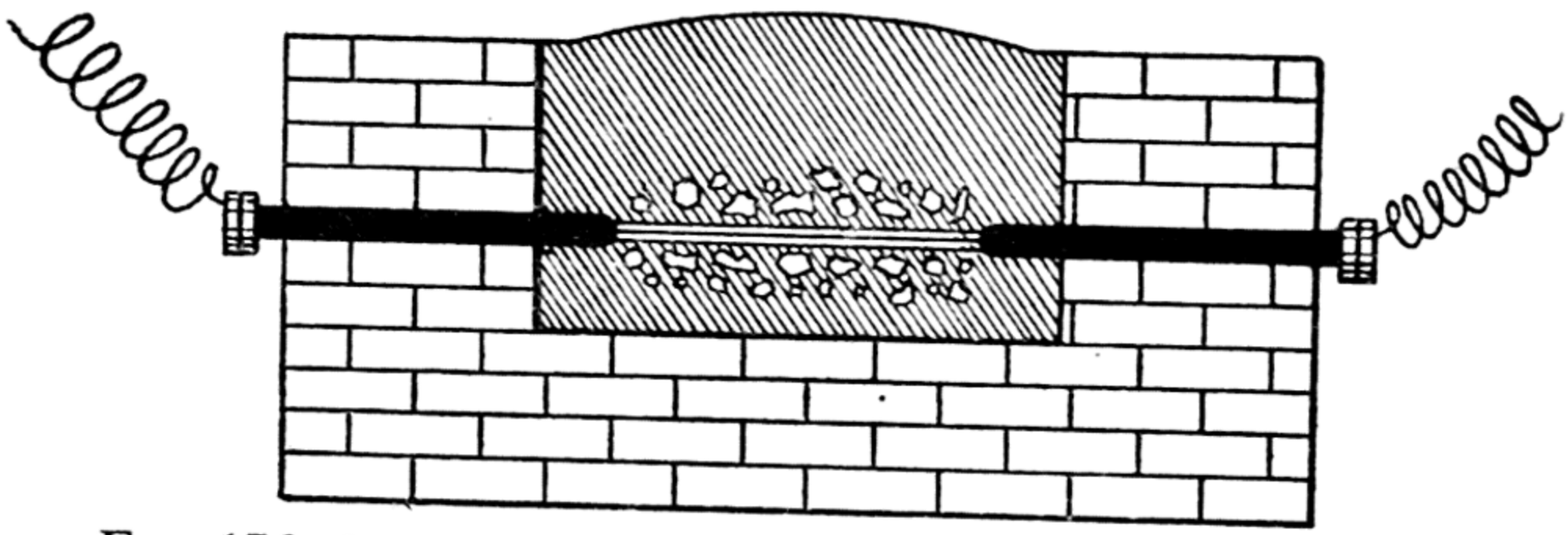


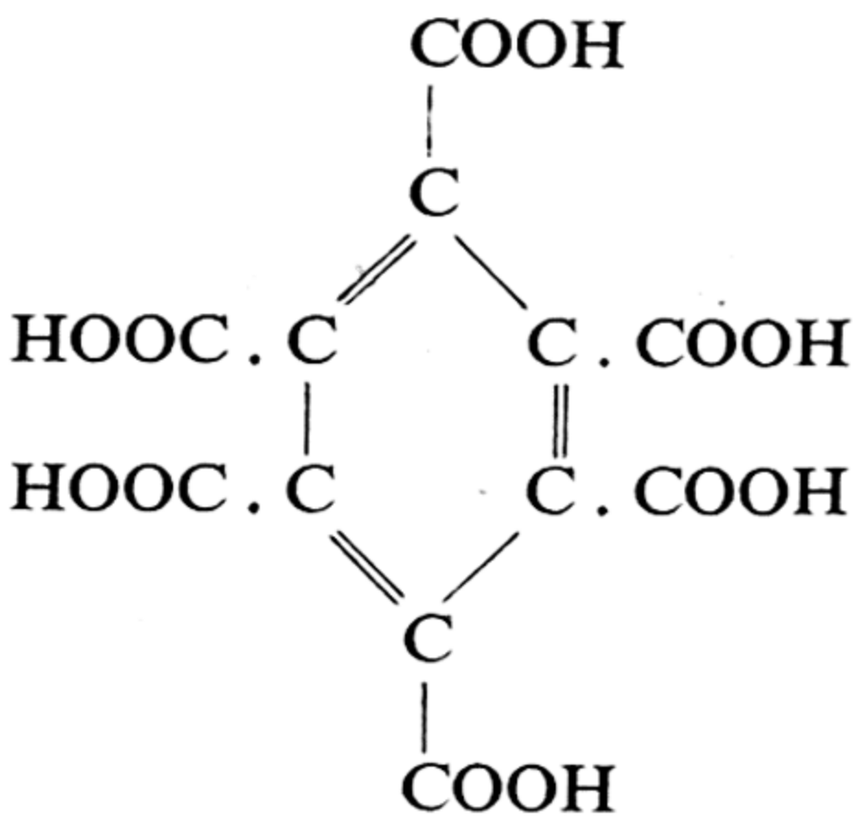
FIG. 176. Manufacture of Graphite by the Acheson Process

structure (*see* p. 558) makes it less dense than the diamond (2·25, cf. 3·5), and it also differs from the diamond in being a good conductor of heat and of electricity, the latter increasing with increase in temperature (with metals, the reverse is the case).

The more open structure of graphite also facilitates its reaction with other chemicals, so that, as might be expected, it is somewhat more reactive chemically than is the diamond. The first stage in its reactions occurs at the weakest points of the structure, that is, between the planes. The action of strong oxidizing agents, such as nitric acid and potassium chlorate for example, causes the graphite to swell in the direction perpendicular to the planes. At the same time, the colour changes to various greens and browns, depending upon the precise conditions, and the metallic lustre and conductivity disappear. These *graphitic oxides* are considered to be graphites in which layers of oxygen atoms (and water molecules) have been introduced chemically between the graphite planes. *Graphitic salts* have a similar structure and are produced for example when graphite is suspended in concentrated sulphuric acid containing a small quantity of an oxidizing agent (such as nitric acid, perchloric acid, chromic anhydride, etc.). These products, which appear blue or purple in transmitted

light and which have a steel-blue lustre, are only stable in the presence of the concentrated acid. With water they are decomposed to reform graphite, which however retains some oxygen. The same type of reactivity is shown when degassed graphite is heated with fluorine at 400°–450°C. A grey solid, of approximate composition CF, is produced in which layers of fluorine atoms are chemically interposed between the layers of carbon atoms. At higher temperatures further reaction occurs and the graphite structure is completely decomposed to form various carbon fluorides.

Graphite is converted by the prolonged action of fuming nitric acid into mellitic acid, which consists of a benzene ring with six carboxyl groups replacing the six hydrogen atoms. When distilled with lime, mellitic acid furnishes benzene. This behaviour may be considered to offer chemical evidence for the six-membered ring-structure of the carbon atoms in graphite.



mellitic acid

Graphite is rather difficult to ignite, but burns when heated in air or in oxygen at about 700°C to form carbon dioxide. It is not attacked by chlorine, by dilute acids nor by fused alkalis.

A substance known as *colloidal graphite* is produced by treating graphite with a strong oxidizing agent such as chromic acid in aqueous solution containing a colloid such as gelatine or tannin. "Aqua-dag" and "Oil-dag" (*dag* = deflocculated Acheson graphite) refer to the suspensions in water and in oil respectively, and these are widely used as lubricants particularly for those parts of machinery which run at temperatures too high for ordinary oils to be used.

The most important uses of graphite are for foundry facings for moulds; graphite (or plumbago) crucibles; lubricants; paints, brushes for electric motors; plates for dry batteries and electrodes for some electrolytic processes (e.g. commercial preparation of fluorine and of chlorine); and in stove polishes. Smaller quantities are used in the manufacture of lead pencils, in electrotyping (when it is used to provide a conducting surface on a non-conducting object, made for example of wood or plastics)

and also in certain rubber compositions. The so-called "lead" of pencils consists of a mixture of soft amorphous graphite, clay, and antimony sulphide which has been baked at a temperature between 800° and 1100°C.

Amorphous Carbon. The numerous forms of amorphous carbon (lamp-black, wood charcoal, animal charcoal, etc.) are all graphitic in character, and are thus not amorphous in the strict sense of the word.

Lamp-black, a very finely divided form of amorphous carbon, is produced commercially by burning petroleum gases or acetylene in a limited supply of air. It is manufactured principally in U.S.A., and is used as a black pigment in printer's ink, paints, and in stove and shoe polishes. Considerable quantities are used in the manufacture of rubber tyres, when it acts both as a filler and as a bonding agent.

Wood charcoal is produced by the destructive distillation of wood—

Wood → { Inflammable gases
Pyroligneous acid (containing acetic acid, methyl alcohol, water, etc.)
Wood tar
Charcoal (the residue)

The wood is heated in closed vessels or retorts in the absence of air, although it is still produced, but on an ever-decreasing scale, by the much less efficient method of charcoal-burning. Billets of wood are stacked in a pile (or *meiler*) and covered with turf to prevent excessive combustion. The pile is then kindled at the centre and after a period of days during which some 80–90 per cent of the original weight of the wood is lost, the pile is dismantled and the charcoal collected.

From the manner in which it is produced it is obvious that charcoal will have a very open porous-like structure. The destructive distillation of the wood drives off numerous volatile products and leaves a skeleton of carbon with an open "honeycomb" structure, the pores of which are occupied by air. It is the presence of this air which gives the charcoal an apparent density of less than one, so that it floats on water. If this air is removed under high vacuum, the charcoal sinks. It is this porous structure of charcoal which also accounts for its most valuable property of adsorbing gases and liquids. Adsorption is essentially a surface phenomenon and should be carefully distinguished from absorption which involves the whole mass of the absorbent, and is therefore a somewhat slower process. Thus we speak of the adsorption of gases by charcoal (that is, surface effect), but of the absorption of a gas by a liquid (that is, solution effect). The adsorption of gases by charcoal is considered to result from some form of chemical attachment of the gas molecules to the surface carbon atoms in the pores of the structure, as a result of which the very considerable internal surface of charcoal becomes covered by a more or less

unimolecular layer of adsorbed gas molecules. The reason why a small piece of charcoal may adsorb many times its own volume of gas (e.g. 170 volumes of ammonia at 0°C) follows from the fact that in the gaseous state each molecule is from ten to fifteen molecular diameters (assuming the molecule to be spherical) away from its nearest neighbour, whereas in the adsorbed state, this distance is reduced to negligible proportions. The effect is not unlike the contraction which occurs when a gas liquefies, when the intermolecular distance is reduced to about two molecular diameters.

The volume of gas adsorbed by charcoal increases—

(*a*) *With decrease in temperature*; charcoal cooled for example in a bath of liquid air is often used to remove residual gases in the production of high vacua. Charcoal at liquid air temperature adsorbs thirteen times the volume of oxygen that it adsorbs at room temperatures.

(*b*) *The higher the boiling point of the gas*, or in other words the more easily the gas condenses. The relationship is not exact, but this preferential adsorption of the more easily condensed gases has proved particularly valuable in gas-masks, since the various poisonous gases are for the most part all much more easily condensed and therefore more readily adsorbed than is oxygen. The gas-mask thus serves to filter out the poisonous gases.

(*c*) *By activating the charcoal* so as to increase the internal surface area. In practice this is usually effected by heating the charcoal with a little steam in the absence of air. Most of the charcoal used industrially is activated by this or other similar methods.

An important result of this adsorption phenomenon is the use of charcoal to catalyze certain gaseous reactions, which either do not occur or else occur only very slowly at ordinary temperatures. For example—

$$H_2 + Cl_2 = 2HCl$$

$$SO_2 + Cl_2 = SO_2Cl_2$$

sulphuryl chloride

$$CO + Cl_2 = COCl_2$$

phosgene

It will be apparent that reaction between two molecules can only occur when the two molecules come into contact with each other, and that in the gaseous state this chance encounter will clearly occur many times less frequently than when the molecules are brought intimately together in the adsorbed state inside the pores of the charcoal. For this reason, charcoal is said to catalyze the above reactions; it speeds up the rate of the reactions so that they occur at ordinary temperatures, and is itself chemically unchanged at the end.

Animal Charcoal, Bone Charcoal, or Bone-char, is made by the destructive distillation of bones in closed retorts. In practice the bones are usually

first degreased with benzene or naphtha and the valuable gelatine then removed by steam or hot water treatment. The products of the destructive distillation include ammonia and other gases, an unpleasant smelling liquid (*Dippel's Oil*) which contains pyridine and certain of the homologues of the latter, and the residue in the retort is animal charcoal. The latter contains about 10 per cent of charcoal which is very finely divided and disseminated through a porous mass of calcium and magnesium phosphates.

Ivory Black is the residue remaining after animal charcoal has been digested with hydrochloric acid to remove the phosphates.

Animal charcoal is heavier and much more easily wetted by liquids than is wood charcoal. It is therefore more suitable than wood charcoal for adsorbing, and so removing, substances in solution. In particular, it is extensively used for removing colouring matter and refining many commercial products. In the refining of sugar, for example, the raw sugar is dissolved in hot water, filtered with the aid of clarifying agents such as infusorial earth, and the filtrate then decolorized by boiling with animal charcoal, before evaporation and crystallization. The product is white sugar. Other examples of this adsorption property include its use to decolorize various waxes, and to remove fusel oil from whisky before the latter is rectified.

Other varieties of amorphous carbon include *gas-carbon*, *coke*, *sugar-carbon* and *soot*. Gas-carbon is a hard form of almost pure carbon. It is deposited on the hot walls of the retorts by the thermal decomposition of hydrocarbons released by the destructive distillation of coal to produce coal gas. Coke is the carbon residue remaining in the retorts. Gas-carbon is a good conductor of electricity and is used to make carbon electrodes for the electric arcs, etc. An increasingly important use of manufactured carbons (Delanium) is in chemical plant manufacture by virtue of their resistance to corrosion, especially by acids, and high thermal conductivity.

Activated Carbon. When amorphous carbon is produced in the normal way by the carbonization (i.e. destructive distillation in the absence of air) of carbonaceous materials (wood, peat, lignite, coal, etc.), its internal surfaces are rendered more or less inactive by the presence of residual tarry products of the distillation. Activation involves cleaning up these internal surfaces and results in an increase in porosity and adsorptive power of the amorphous carbon. This process is further enhanced by an increase in the internal surface area which accompanies the cleaning-up treatment.

The processes for producing activated carbon commercially include—

(*a*) *Gas Activation Processes.* The carbon is heated in air at 350° to 500°C and then with superheated steam at 800° to 1000°C. The activity of the final product increases with the time of steaming, but results in a decreasing yield and lower bulk-density.

(*b*) *Chemical Activation Processes.* The raw material (wood, saw-dust,

lignite, etc.) is impregnated with zinc chloride or syrupy phosphoric acid before carbonization. The zinc-chloride-impregnated material is then carbonized at a temperature between 400° and 600°C, and the product treated with acid to leach out the residue of zinc oxide. The phosphoric acid treated material is carbonized for 8 to 10 hours at a final temperature of approximately 1000°C. Oxidation of the tarry matter occurs and the phosphoric acid is reduced to phosphorus which distils off.

Chemical Properties of Amorphous Carbon. Chemically, amorphous carbon is more reactive than diamond and graphite, and reactions occur at a correspondingly lower temperature. It combines directly with oxygen on heating to form carbon dioxide, with fluorine to form carbon tetrafluoride, but not with chlorine, bromine, or iodine. The absence of flame in these reactions is a necessary consequence of the practically non-volatile nature of carbon (*see* p. 557). Small quantities of various hydrocarbons may be produced by heating carbon in hydrogen at high temperatures and pressures. Direct reaction occurs between sulphur vapour and carbon at the temperature of an electric furnace to form carbon disulphide, and between silicon and carbon in the electric furnace to form carborundum. Some metals combine directly with carbon at very high temperatures to form carbides (e.g. CaC_2, Al_4C_3, Fe_3C).

At sufficiently elevated temperatures, carbon is a powerful reducing agent. Thus, it reduces many metallic oxides to the metal (e.g. CuO, PbO, SnO, ZnO and Fe_2O_3, but not the oxides of the alkali and alkaline earth metals); reduces steam to hydrogen as in the production of water-gas (*see* p. 573); reduces carbon dioxide to carbon monoxide; reduces hot concentrated sulphuric acid and also hot concentrated nitric acid—

$$C + 2H_2SO_4 = 2H_2O + 2SO_2 + CO_2$$
$$C + 4HNO_3 = 2H_2O + 4NO_2 + CO_2$$

and may react explosively with solid oxidizing agents such as potassium perchlorate, potassium chlorate, potassium nitrate, etc. Gunpowder is a mixture of about 75 per cent of potassium nitrate, 10 per cent of sulphur, and 15 per cent of charcoal; *ophorite*, a mixture of potassium perchlorate and charcoal, is dangerously explosive.

Oxides of Carbon

Carbon Dioxide, CO_2. The usual laboratory method of preparation is to treat marble chips with dilute hydrochloric acid. The reaction occurs in the cold and may be carried out in a Kipp's apparatus—

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

The gas may be dried by concentrated sulphuric acid, phosphorus pentoxide or calcium chloride, and (since it is moderately soluble in water) is collected by the upward displacement of air.

Carbon dioxide is liberated by the action of heat on any metallic carbonate (except sodium, potassium, or barium carbonates), bicarbonate or basic carbonate—

$$CaCO_3 = CaO + CO_2$$
$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$
$$CuCO_3 . Cu(OH)_2 = 2CuO + H_2O + CO_2$$

The combustion of carbon or its compounds in excess of air or oxygen, reactions which recall the part played by carbon dioxide in the "carbon cycle" (*see* p. 555), also gives rise to carbon dioxide—

$$C + O_2 = CO_2$$
$$2CO + O_2 = 2CO_2$$
$$\underset{\text{methane}}{CH_4} + 2O_2 = CO_2 + 2H_2O$$

Industrially, carbon dioxide is produced in large quantities in—

(*a*) The manufacture of quick-lime by burning limestone in lime-kilns, (*see* p. 502)—

$$CaCO_3 = CaO + CO_2$$

(*b*) The fermentation processes for producing alcohols (and other compounds) from sugars, etc. The reactions are complex, and the products vary with the particular strain of enzyme used (*see* p. 896). In the brewing industry, for example, a particular strain of enzyme is used to ferment sugar to alcohol, the net reaction being expressed by the equation—

$$\underset{\text{sugar}}{C_6H_{12}O_6} = 2\underset{\text{alcohol}}{C_2H_5OH} + 2CO_2$$

The carbon dioxide is absorbed under pressure in a solution of potassium carbonate—

$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3$$

and the gas subsequently recovered pure by reversing the pumps and so reducing the pressure or by boiling the bicarbonate solution. The same solution of potassium carbonate may thus be used repeatedly. The carbon dioxide so purified is sold commercially as the liquid under pressure in steel cylinders, or in the form of solid blocks, when it is known as "Cardice" or "Drikold."

Properties of Carbon Dioxide. Carbon dioxide is a colourless, odourless gas, moderately soluble in water to form a slightly acid solution, and is not poisonous (although it does not support respiration and high concentrations produce asphyxiation). It was first liquefied by Faraday in 1823 by the combined action of pressure and reduced temperature. Later, Andrews in his investigations on the liquefaction and critical phenomena of gases showed that if the temperature is above 31·1°C (the critical temperature),

carbon dioxide cannot be liquefied no matter how high the pressure. Liquid carbon dioxide is a colourless mobile liquid, and is only stable under pressure, as indicated in the accompanying equilibrium diagram.

When liquid carbon dioxide is allowed to flow from an inverted carbon dioxide cylinder into an open vessel, or better into a cloth bag, the heat absorbed by the rapid evaporation of a portion of the carbon dioxide solidifies the remainder to produce a white, snow-like mass of solid carbon dioxide. Commercially, this "snow" is compressed hydraulically into blocks of dry ice, etc. Only about 30 per cent of the liquid carbon dioxide is solidified in this way, but the remainder is reliquefied and the process repeated. Solid carbon dioxide evaporates without melting at −78°C, but it may be liquefied if the pressure is increased to about five atmospheres. The reason why solid carbon dioxide does not evaporate rapidly in air at ordinary temperatures is due partly to its high latent heat (87·2 cal./g) and partly to the fact that it surrounds itself with a protecting blanket of heavy carbon dioxide gas. It may therefore be stored for long periods and distributed by rail, etc., without appreciable evaporation losses. It is used as a refrigerant both in the solid form and also when added to organic liquids with low boiling points (e.g. acetone, ether, etc.). Ether, for example, may be cooled in this way to about −110°C in air, or to −140°C under reduced pressure, the lower temperature in the latter case resulting from the more rapid evaporation of the carbon dioxide.

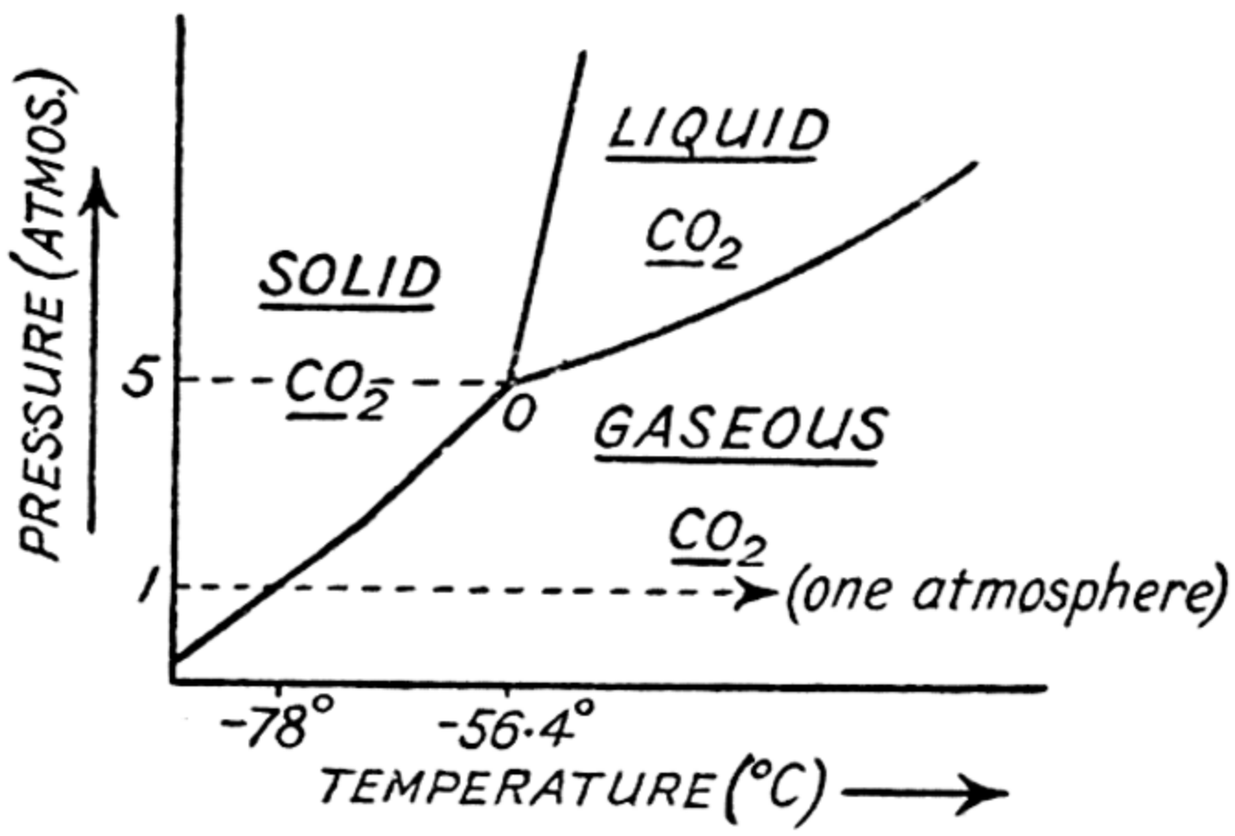


FIG. 177. Equilibrium Diagram for Carbon Dioxide

Examples of the uses of solid carbon dioxide include the storage and transport of ice-cream, the preservation of foodstuffs (fish, etc.) being transported over long distances, the manufacture of mineral waters, and in industry in the shrinkage fitting of machine parts.

The solubility of carbon dioxide in water increases considerably with increase in pressure. Thus, in the Bosch process for manufacturing hydrogen (*see* p. 367), the carbon dioxide is almost completely removed by washing with water under 25–50 atmospheres pressure. Mineral-water and "soda-water" contain carbon dioxide in solution under pressure. When the pressure is released the solution effervesces due to the escape of the gas from solution.

Carbon dioxide does not burn nor support combustion, and this property accounts for its use in certain types of portable fire-extinguishers.

One type contains a dilute solution of sodium bicarbonate and a vessel containing sulphuric acid. When the fire-extinguisher is inverted the two solutions come into contact, and the pressure developed by the resulting liberation of carbon dioxide forces the still reacting liquids and dissolved carbon dioxide out through the delivery jet. A blanket of relatively heavy carbon dioxide thus tends to isolate the flames from the oxygen of the air, and the fire is extinguished. Portable fire extinguishers containing carbon dioxide under pressure are also in extensive use. Carbon dioxide will, however, support the combustion of sodium, potassium and magnesium, if these are first ignited before plunging into the gas; the heat of the burning metal probably first decomposes the carbon dioxide into carbon and oxygen, the latter then supporting the continued combustion of the metals.

$$4K + 3CO_2 = 2K_2CO_3 + C$$

$$2Mg + CO_2 = 2MgO + C$$

The slightly acidic character of the solution of carbon dioxide in water is thought to be due to the formation of carbonic acid—

$$H_2O + CO_2 = H_2CO_3$$

although this acid is too unstable to isolate. It is, however, the parent acid of the numerous metallic carbonates, bicarbonates and basic carbonates, and is dibasic. The following reactions occur, for example, when carbon dioxide is passed into a solution of sodium hydroxide—

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

$$Na_2CO_3 + H_2O + CO_2 = \underset{\text{sodium bicarbonate}}{2NaHCO_3}$$

With lime-water, instead of sodium hydroxide, the first formed calcium carbonate is insoluble and the solution therefore turns milky. With further passage of carbon dioxide, the soluble calcium bicarbonate forms and the solution turns clear again. These reactions are those involved in the familiar lime-water test for carbon dioxide—

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

Sodium, potassium and barium carbonates are not decomposed by heating, but other carbonates decompose on heating to liberate carbon dioxide (magnesium, calcium and lithium carbonates, however, require fairly high temperatures)—

$$CaCO_3 = CaO + CO_2$$

All bicarbonates decompose on heating (below 100°C) to form the

normal carbonates, and these may then decompose further at higher temperatures, as described above.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

$$Ca(HCO_3)_2 = CaO + 2CO_2 + H_2O$$

The carbonates of sodium, potassium and ammonium are soluble in water, but all the others are insoluble; the bicarbonates are all soluble, but those of sodium and potassium are amongst the least soluble. The insoluble carbonates are usually prepared by double decomposition with aqueous sodium carbonate, e.g.—

$$FeSO_4 + Na_2CO_3 = FeCO_3\downarrow + Na_2SO_4$$

but with metals lower in the electrochemical series (e.g. copper and lead), a basic carbonate such as $CuCO_3 . Cu(OH)_2$ is precipitated instead of the normal carbonate. Normal magnesium carbonate is precipitated on adding a solution of sodium bicarbonate saturated with carbon dioxide to a solution of a magnesium salt.

All these carbonates, bicarbonates and basic carbonates effervesce when treated with a dilute acid. Some natural carbonates, such as magnesite, $MgCO_3$, siderite, $FeCO_3$, and dolomite, $CaCO_3 . MgCO_3$, do not react appreciably in the cold, but reaction occurs rapidly with the powdered minerals on warming. Only the very weak acids, such as boric acid, hydrogen sulphide, and hydrocyanic acid do not react in this way.

A bicarbonate may be distinguished from a normal carbonate by such tests as—

(*a*) Add a solution of magnesium sulphate to a cold solution of the carbonate or bicarbonate. If a white precipitate is formed immediately, then the solution contains a normal carbonate, but if the white precipitate only forms on boiling, then it contains a bicarbonate—

$$Na_2CO_3 + MgSO_4 = Na_2SO_4 + MgCO_3\downarrow$$

$$2NaHCO_3 + MgSO_4 = \underset{\text{soluble}}{Mg(HCO_3)_2} + Na_2SO_4$$

$$Mg(HCO_3)_2 \xrightarrow{\text{boil}} MgCO_3\downarrow + CO_2 + H_2O$$

(*b*) Boil the unknown solution. If carbon dioxide is evolved (lime-water test), a bicarbonate is present.

(*c*) Add a solution of mercuric chloride. Normal carbonates give a reddish brown precipitate of a basic mercuric carbonate in the cold, whereas bicarbonates only give the precipitate on boiling.

To detect a bicarbonate in presence of a carbonate, the usual method is to add excess of calcium chloride to precipitate the normal carbonate as calcium carbonate and convert the bicarbonate into calcium bicarbonate. The calcium carbonate is filtered off, and the filtrate then treated with

ammonium hydroxide. The formation of a white precipitate then indicates the presence of a bicarbonate—

$$Ca(HCO_3)_2 + 2NH_4OH = CaCO_3\downarrow + (NH_4)_2CO_3 + 2H_2O$$

Composition of Carbon Dioxide. That carbon dioxide contains only carbon and oxygen is established by the formation of the gas when pure carbon is burnt in oxygen. If the experiment is carried out by heating a piece of charcoal in a confined volume of oxygen, for example in a eudiometer (*see* Fig. 178), then when the original temperature condition has been restored it is found that there is no resultant change in volume. Thus—

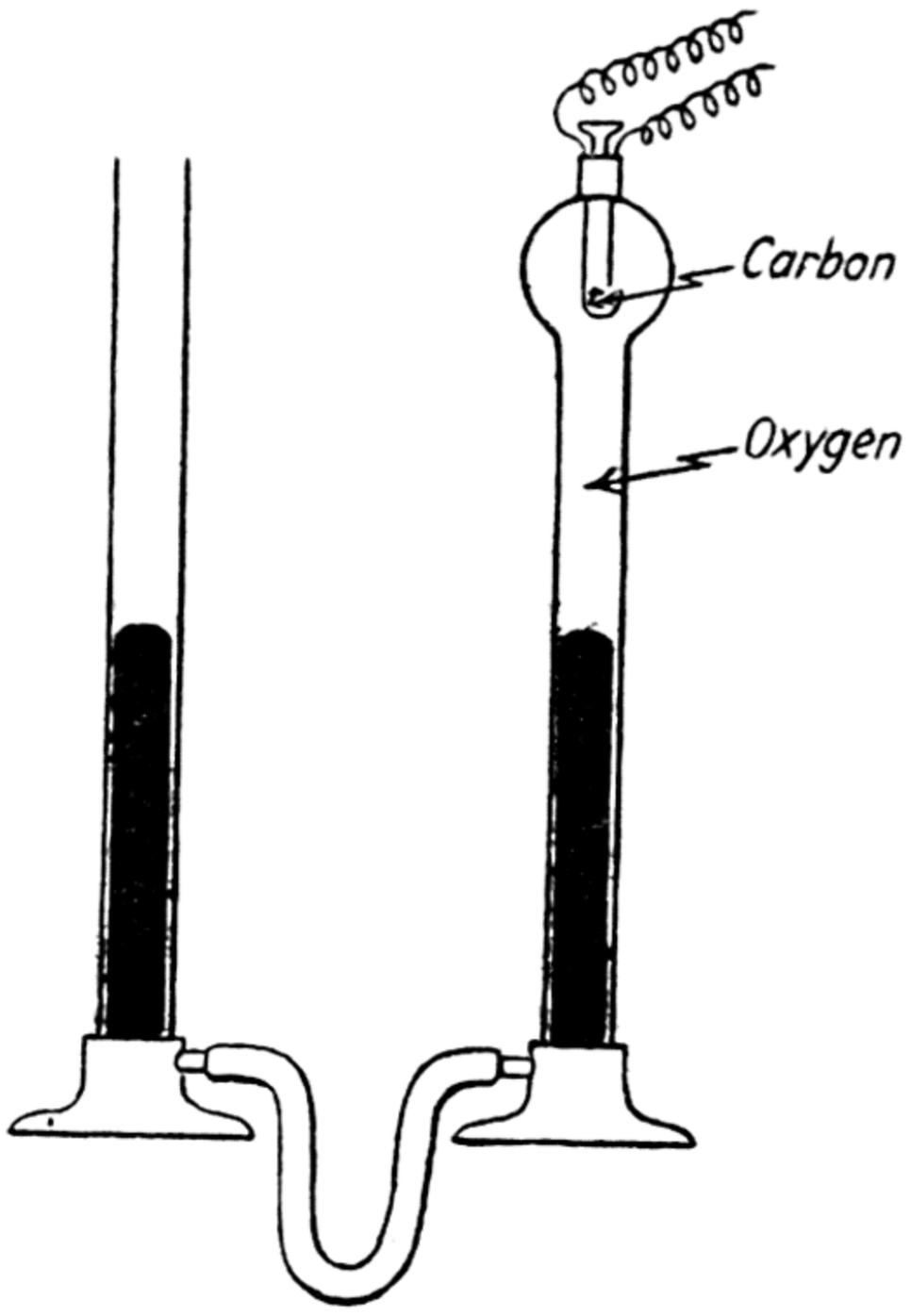


FIG. 178. Eudiometer for Determination of Carbon Dioxide by Volume

$$\text{Carbon} + 1 \text{ volume of } O_2 \rightarrow 1 \text{ volume of } C_xO_y$$

whence, by Avogadro's hypothesis—

$$\text{Carbon} + O_2 \rightarrow C_xO_y$$

so that the formula of carbon dioxide is C_xO_2.

The same result may be obtained gravimetrically by burning a weighed amount of carbon (sugar charcoal, etc.) in a stream of carbon dioxide-free air and finding the weight of the resulting carbon dioxide by absorption in weighed potash bulbs, as shown in Fig. 178.

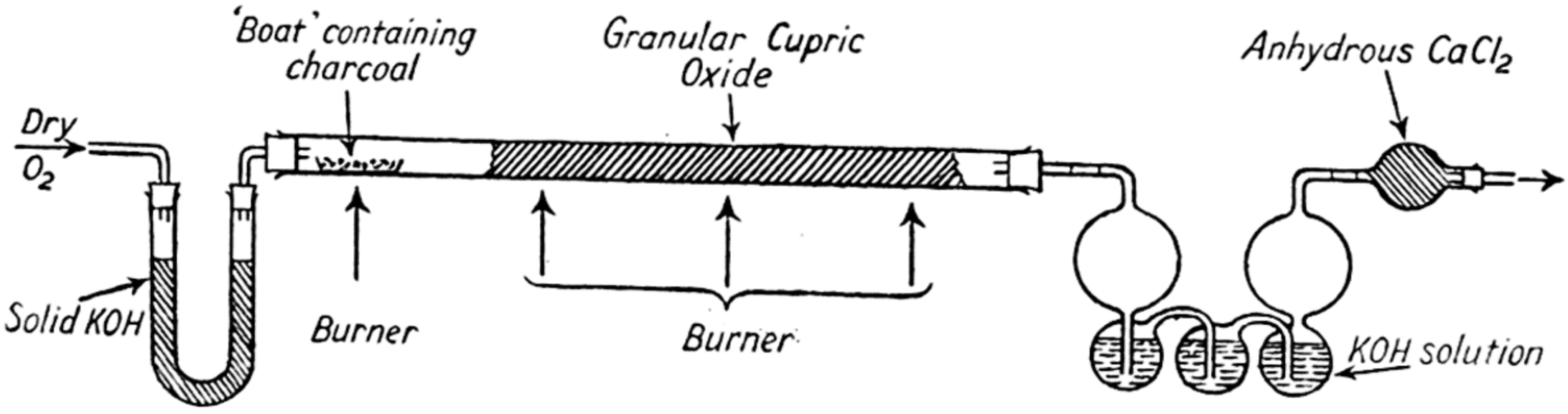


FIG. 179. Apparatus for Determining the Composition of Carbon Dioxide by Weight

The column of granular cupric oxide, which is maintained at red-heat throughout the combustion, serves to oxidize any carbon monoxide to carbon dioxide. The experiment shows that 3·00 g of carbon combine

with 8·00 g of oxygen to form carbon dioxide, the equivalent weight of carbon being therefore 3·00. Since the molecular weight of carbon dioxide, as determined from its vapour density, is 44, this result shows that each gramme-molecule contains 12 g of carbon and 32 g of oxygen, and hence that its molecular formula is C_xO_2 (since the atomic weight of oxygen is 16).

To determine x, it is necessary to know the atomic weight of carbon. This has been determined by Cannizzaro's method (*see* p. 34) and shown to be 12. Since, therefore, one gramme molecule of C_xO_2 contains 12 g of carbon, it follows that x equals one, and that the molecular formula of carbon dioxide is CO_2.

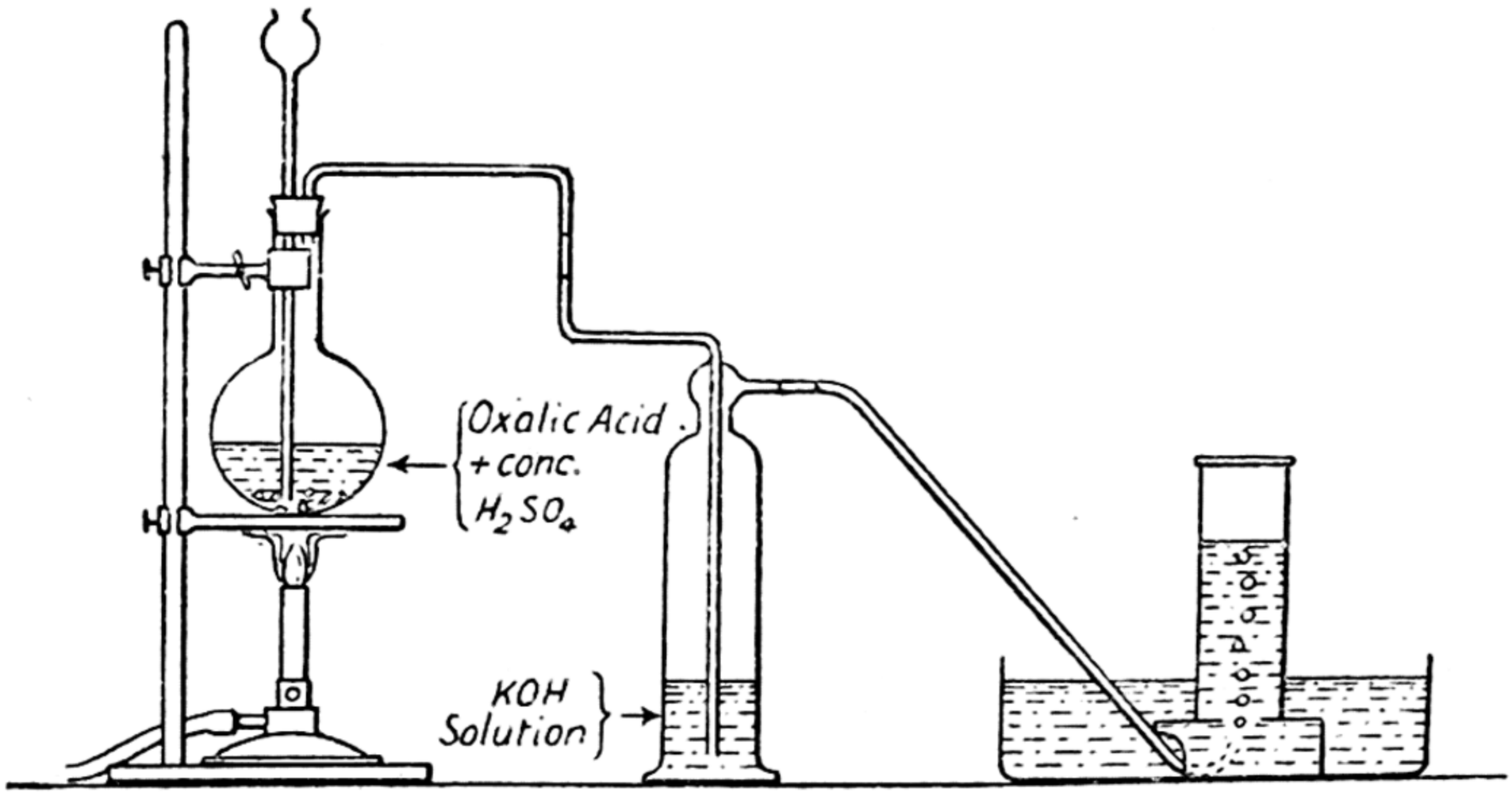


FIG. 180. Preparation of Carbon Monoxide from Oxalic Acid

Uses of Carbon Dioxide. Many of the uses of solid carbon dioxide have already been mentioned on p. 568. Other uses of carbon dioxide gas include the manufacture of sodium carbonate by the Ammonia-Soda process (*see* p. 432), the preparation of mineral and soda-waters, the manufacture of "white-lead," in fire extinguishers, and also in the solid form as a refrigerant. The latter delays bacterial decomposition of food-stuffs not only because of the low temperature produced but also because bacteria do not thrive in an atmosphere of carbon dioxide.

Carbon Monoxide, CO. The usual laboratory method is to remove the elements of water from formic acid or oxalic acid by the action of concentrated sulphuric acid and warming—

Formic acid $\quad H\,.\,COOH - H_2O = CO$

Oxalic acid $\quad \begin{matrix} COOH \\ | \\ COOH \end{matrix} - H_2O = CO + CO_2$

A suitable form of apparatus is shown on p. 572, and includes a wash-bottle containing a strong solution of potassium hydroxide to remove the carbon dioxide and traces of sulphur dioxide. The carbon monoxide is collected over water, but may be dried by means of calcium chloride, concentrated sulphuric acid or phosphorus pentoxide and then collected over mercury.

Carbon monoxide may also be prepared—

(*a*) By heating potassium ferrocyanide with excess of concentrated sulphuric acid. The reactions are complex and probably involve the intermediate liberation of hydrocyanic acid (HCN) which is hydrolyzed to form ammonia and formic acid. The ammonia is fixed by the sulphuric acid as ammonium sulphate, and the formic acid then liberates carbon monoxide by the reaction described above—

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O =$$
$$2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO \uparrow$$

(*b*) By passing carbon dioxide through a long tube containing carbon heated to redness. The latter reduces the carbon dioxide to form carbon monoxide, and any unreduced carbon dioxide is removed by passing through a wash-bottle containing potassium hydroxide solution.

$$CO_2 + C = 2CO$$

Note—The reverse process of oxidizing carbon monoxide to carbon dioxide is effected by passing carbon monoxide through a column of granular cupric oxide heated to redness—

$$CO + CuO = Cu + CO_2$$

(*c*) By a modification of (*b*), in which oxygen is used instead of carbon dioxide. The oxygen is converted to carbon dioxide in the first part of the carbon column, and this is then reduced to carbon monoxide as in (*b*)—

$$C + O_2 = CO_2$$
$$CO_2 + C = 2CO$$

Industrially, carbon monoxide is produced in very large quantities in the form of various gaseous fuels, such as producer gas, water gas, semi-water gas, carburetted water gas, blast-furnace gas and coal gas. These are discussed in detail later (*see* p. 594), but the following brief notes are included here for reference.

Producer gas is a mixture of carbon monoxide and nitrogen produced by blowing air through red hot coke at a temperature of about 1000°C. The reaction is exothermic.

Water gas is produced by the endothermic reaction of steam on coke at

high temperatures (1200°–1400°C) and contains carbon monoxide and hydrogen as the principal constituents.

$$C + H_2O = CO + H_2 - 29\,000 \text{ cal.}$$

A small quantity of carbon dioxide is also produced, but the amount becomes insignificant at very high temperatures—

$$C + 2H_2O = CO_2 + 2H_2 - 19\,000 \text{ cal.}$$

Semi-water gas is virtually a mixture of producer gas and water gas and is produced by passing air and steam together over coke heated to about 1000°C. The proportion of air to steam is so regulated that the heat evolved by the producer gas reaction compensates for the heat absorbed by the water gas reaction, so that the coke remains red hot.

Carburetted water gas consists of water gas together with various gaseous hydrocarbons, and is produced by heating water gas, into which is injected a fine spray of oil, to about 750°C. The oil breaks down under the heat treatment to form simple hydrocarbons, such as methane (CH_4), ethylene (C_2H_4), etc., which are gases at ordinary temperature.

Coal gas contains about 8 per cent of carbon monoxide and is produced by the destructive distillation of coal. The principal constituents of coal gas are hydrogen and methane.

TABLE 90

Approximate Percentage Composition of Gaseous Fuels with their Calorific Values

Fuel	CO	H_2	N_2	CO_2	Hydrocarbons	Calorific Value (B.Th.U./ft³)
Producer Gas . .	23	18	49	6	4	180
Water gas . . .	43	47	5	4	1	300
Carburetted water gas .	36	38	4	4	18	470
Blast furnace gas . .	28	3	57	11	1	100
Coal gas . . .	8	53	6	2	31	530

Properties of Carbon Monoxide. Carbon monoxide is a colourless, odourless gas, approximately the same density as air (14·0, cf. 14·4), and is practically insoluble in water. It is extremely poisonous since it combines with the haemoglobin of the blood to form carboxy-haemoglobin, and so prevents the red blood corpuscles from supplying oxygen (via oxy-haemoglobin) from the lungs to other parts of the body. This deficiency of oxygen leads to a form of suffocation, and death. Concentrations of carbon monoxide less than one per cent prove fatal if inhaled for any moderate length of time, (0·02 per cent is associated with the first slight

symptoms of poisoning on prolonged exposure). Carbon monoxide *is* particularly dangerous because of its absence of odour, so that its presence may not be suspected until too late. It is present in "after-damp," the gas present in coal mines after an explosion, and results from the incomplete combustion of "fire-damp" (methane). Carbon monoxide is in fact produced in practically all cases of incomplete combustion of carbon compounds, for example, in the exhaust gases from petrol engines, in coal gas, and in coke fires. Various unpleasant smelling gases are deliberately left in, or even added to, coal gas so that any leakage may readily be noticed, but it should be noted that the olfactory organs quickly become dulled so that after a time coal gas loses its unpleasant odour and fatal accidents may then occur.

Carbon monoxide burns in air with a characteristic blue flame to form carbon dioxide. This blue flame may often be seen above a clear-burning coal fire, the carbon monoxide being formed by the reduction of the first formed carbon dioxide as it passes upwards through the hot coals—

$$C + O_2 = CO_2$$
$$CO_2 + C = 2CO$$

Mixtures of carbon monoxide and oxygen (or air) may explode when sparked, but if the gases are very thoroughly dried explosion is said not to occur.

Carbon monoxide is classified as a neutral oxide, since it does not react under ordinary conditions with either acids or bases. It does, however, react with solid sodium hydroxide at about 200°C under pressure to form sodium formate, a reaction which is now carried out on a commercial scale—

$$NaOH + CO = H\,.\,COONa$$

sodium formate

This reaction recalls the concentrated sulphuric acid method for preparing carbon monoxide from formic acid. The reaction is not, however, reversible, and carbon monoxide is not therefore regarded as an acidic oxide.

Carbon monoxide has the structure $C \overleftarrow{\equiv} O$ in which each atom has acquired its full complement of electrons; oxygen acquires the necessary two additional electrons from the double bond, and carbon acquires its four electrons, two from the double bond and two from the co-ordinate link. Carbon monoxide, however, forms a number of interesting addition compounds, and in these reactions it appears to behave as if it had the structure

$$\rangle C{=}O, \quad \text{or} \quad \leftarrow C \overleftarrow{\equiv} O$$

Presumably, the carbon monoxide changes to the former reactive form

under the polarizing forces of the other compound immediately before the addition reaction. Examples of these addition reactions include—

(*a*) The addition of carbon monoxide to chlorine in the presence of sunlight or charcoal to form phosgene, $COCl_2$—

$$CO + Cl_2 = \begin{matrix} Cl \\ \\ Cl \end{matrix}\!\!\diagdown\!\!\diagup C{=}O$$

carbonyl chloride

(*b*) The solution of carbon monoxide in ammoniacal or hydrochloric acid solution of cuprous chloride to form the compound, $CuCl \cdot CO \cdot 2H_2O$. This reaction is used in gas analysis to absorb carbon monoxide from a mixture of gases.

(*c*) The addition of carbon monoxide to certain metals (particularly such metals as nickel which can be prepared in a reactive form by reduction of the oxide at comparatively low temperatures) to form a class of compound known as *metallic carbonyls*. Examples include—

Nickel carbonyl, $Ni(CO)_4$—a colourless liquid, b. p. 43°C.

Cobalt carbonyl, $Co_2(CO)_8$—orange solid, m. p. 51°C.

Iron carbonyls, e.g. $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$.

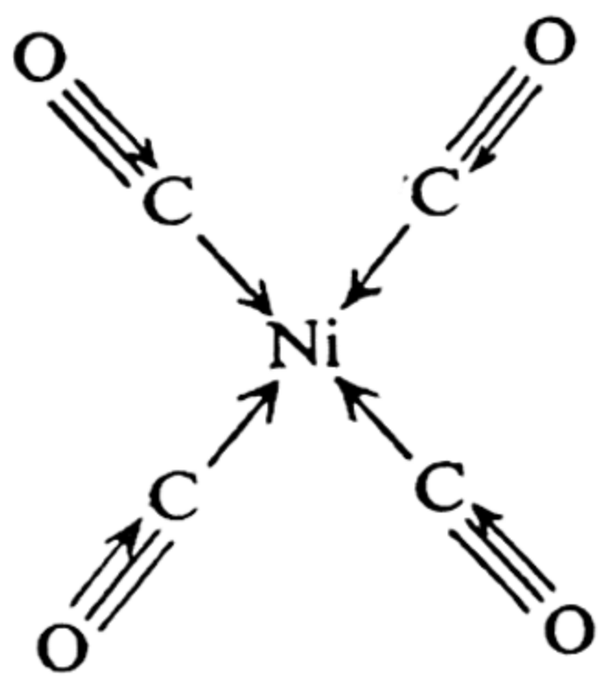


FIG. 181. Nickel Carbonyl

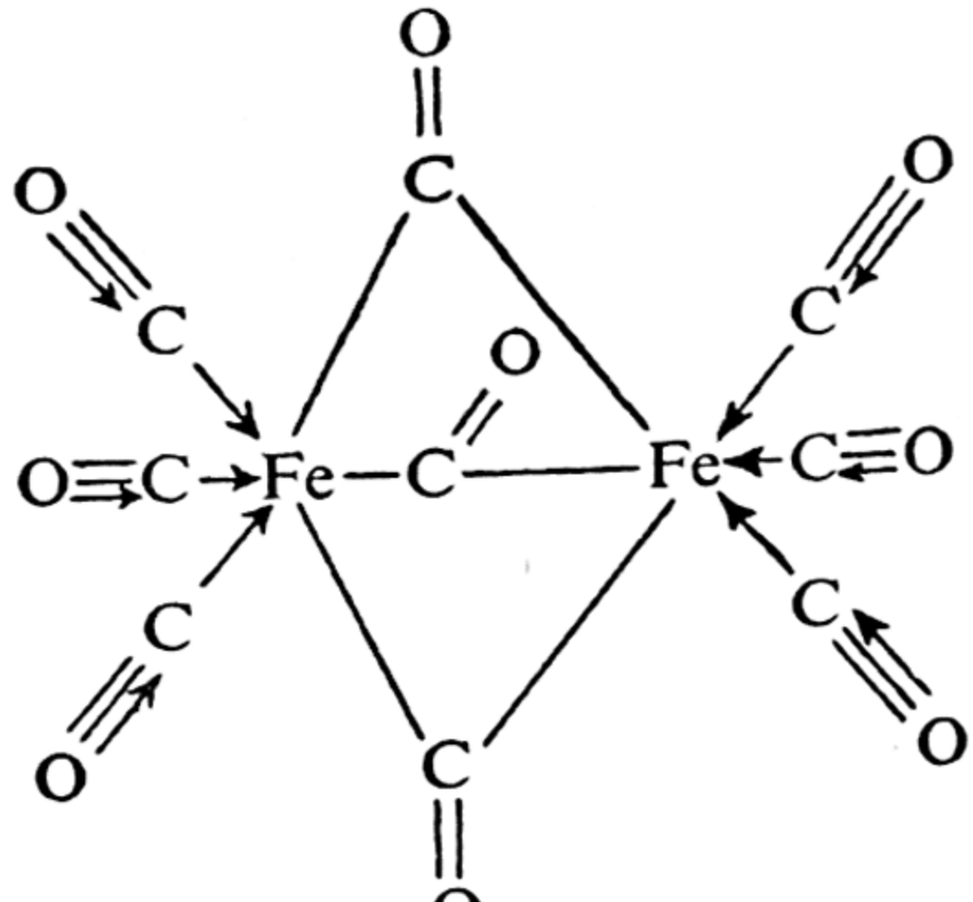


FIG. 182. Iron Nonacarbonyl

These metallic carbonyls are characterized by their ready volatility, and this property has proved particularly important in the purification of nickel in the *Mond nickel process*. The oxide is reduced under controlled conditions, and the crude metal then treated with carbon monoxide gas at about 50°C at atmospheric pressure (at this pressure cobalt does not form a carbonyl). The resulting nickel carbonyl is carried away (as a gas) by the circulating gas into "decomposers," maintained at a temperature of 180–200°C. The nickel carbonyl decomposes and deposits the nickel

on small pellets of nickel (2–5 mm diameter) which are made to fall down the tower. The product is 99·8 per cent pure nickel and is free from cobalt impurity but does contain about 0·25 per cent of iron due to the simultaneous formation and volatilization of iron carbonyl.

(*d*) The alkali and alkaline-earth metals form a different and much less important class of "carbonyl" with carbon monoxide, and mention will be made only of one of these compounds, namely, *potassium carbonyl*. This compound, having the composition $(KCO)_n$, is produced as an explosive by-product in the old method of producing potassium by reduction of the carbonate at high temperatures with carbon. It was later shown that potassium absorbs carbon monoxide at about 80°C to form $K_6(CO)_6$. This compound is not, however, a true carbonyl; it is the potassium salt of hexahydroxy-benzene, $C_6(OH)_6$, which it forms when treated with dilute hydrochloric acid.

Carbon monoxide is a reducing agent. At room temperatures, it reduces Fehling's solution to cuprous oxide and ammoniacal silver nitrate to metallic silver. At elevated temperatures it reduces oxides of the baser metals (e.g. PbO, CuO, FeO) to the metal, a reaction which occurs, for example, in the blast furnace—

$$FeO + CO = Fe + CO_2$$

It will not, however, reduce oxides of the metals in the upper half of the electrochemical series (MgO, Al_2O_3, CaO, etc.). It reduces iodine pentoxide to liberate iodine, the easy detection of which makes this reaction one of the standard and easiest methods for detecting carbon monoxide in a mixture of gases

$$I_2O_5 + 5CO = I_2 + 5CO_2$$

Detection of Carbon Monoxide. The usual laboratory method is the iodine pentoxide reaction mentioned above. One form of portable apparatus uses iodine pentoxide in admixture with sulphuric acid. Other methods include the "hopcalite" method, in which the carbon monoxide is catalytically oxidized by a mixture of the oxides of copper, manganese, cobalt and silver; the use of red mercuric oxide in which the liberated mercury is estimated by a test-paper impregnated with selenium sulphide; and the more recent methods developed during the war which use palladium compounds on a silica-gel base. The latter is impregnated with potassium pallado-sulphite, which is yellow and changes to dark brown in the presence of carbon monoxide.

Composition and Formula of Carbon Monoxide. That carbon monoxide contains only carbon and oxygen is indicated by the fact that it burns in oxygen to form carbon dioxide. If this reaction is carried out in a eudiometer, it is found that—

$$2 \text{ volumes } C_xO_y + 1 \text{ volume } O_2 \rightarrow 2 \text{ volumes } CO_2$$

whence, by Avogadro's hypothesis—

$$2C_xO_y + O_2 = 2CO_2$$

so that the molecular formula of carbon monoxide is CO.

Carbon Suboxide, C_3O_2. Carbon suboxide was first prepared by heating a mixture of diethyl malonate with a large excess of phosphorus pentoxide at about 300°C, but it may also be prepared from malonic acid by the same method—

$$\begin{matrix} COOH \\ | \\ CH_2 \\ | \\ COOH \end{matrix} \quad - 2H_2O = C_3O_2$$

It is a gas at room temperatures (b. p. 6°C, m. p. − 111°C), has a pungent odour and is poisonous. The mixture with oxygen explodes when ignited to form carbon dioxide. It reacts with cold water to form malonic acid, and is therefore regarded both as a sub-oxide and as the anhydride of malonic acid.

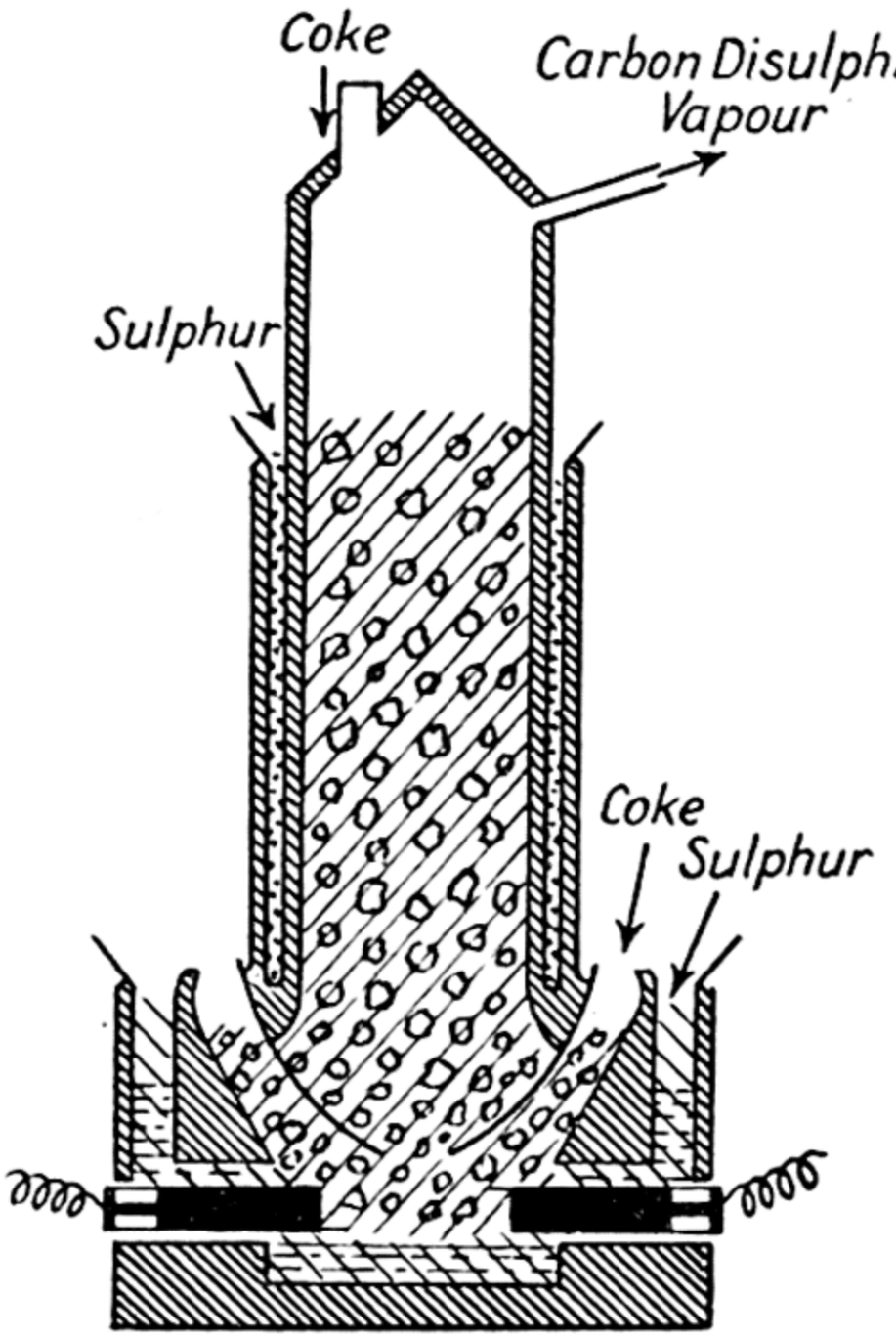


FIG. 183. Manufacture of Carbon Disulphide

Hydrocarbons. Carbon forms a very large number of compounds with hydrogen, and many of these compounds are described in the Organic Chemistry section of this book, for example in Chapters 27 and 37. The student should, however, familiarize himself at this stage with the simpler hydrocarbons, such as methane (CH_4, p. 870), ethylene (C_2H_4, p. 859) and acetylene (C_2H_2, p. 878), since a knowledge of these three hydrocarbons is of considerable value in understanding the inorganic chemistry of Carbon.

Carbon Disulphide, CS_2, is a colourless liquid, which is prepared commercially by the action of sulphur vapour on carbon at very high temperatures in an electric furnace as shown in the accompanying diagram—

$$C + 2S = CS_2 - 21\,000 \text{ cal.}$$

Two pairs of carbon electrodes are inserted symmetrically into the circular hearth of the furnace. Coke is fed through four hoppers, arranged one above each electrode. Above the hearth is a tower packed with coke which is heated from the hearth. The tower and the hearth are jacketed

by channels containing sulphur (fed in through hoppers at the top) which effectively insulates the tower and supplies molten sulphur to the well in the hearth of the furnace, where it is volatilized. The sulphur vapour passes upwards through the incandescent carbon with which it reacts to form carbon disulphide. The carbon disulphide vapour passes out at the top of the furnace to suitable condensers. Temperature regulation in the furnace is largely automatic; increase in temperature causes more sulphur to melt and flow to the hearth where it rises and partially covers the carbon electrodes. Since sulphur is a non-conductor, this is equivalent to reducing the effective surface of the electrodes so that the temperature falls.

Carbon disulphide is a colourless liquid, boiling at 46°C. As normally prepared it has a most unpleasant odour, but when purified by shaking with mercury or lead acetate, it has a smell not unlike that of chloroform. The unpleasant smell, however, soon returns. The vapour is both poisonous and very inflammable, and forms explosive mixtures with air and also with nitric oxide (*see* p. 652)—

$$2CS_2 + 5O_2 = 2CO + 4SO_2$$
$$2CS_2 + 10NO = 2CO + 4SO_2 + 5N_2$$

The very low ignition temperature of carbon disulphide vapour and the ease with which the liquid vaporizes, make carbon disulphide one of the most dangerously inflammable liquids normally used in the laboratory. Small quantities only should be used at a time, and the storage bottle kept in a cool place away from flames.

The uses of carbon disulphide are numerous; it dissolves sulphur, phosphorus, iodine, essential oils, rubber, gums and resins, and also alkaloids. It is used extensively in the manufacture of carbon tetrachloride (*see* p. 580) and in the production of viscose artificial silk.

In the production of viscose, the cellulose (wood pulp or cotton pulp) is treated with sodium hydroxide solution to form alkali celluloses such as $C_6H_9O_4(ONa)$ (empirical formula)—

$$C_6H_{10}O_5 + NaOH = C_6H_9O_4(ONa) + H_2O$$

This alkali cellulose is then separated from the excess alkali by filtration and hydraulic presses to form sheets of alkali cellulose. These are converted into a fluffy form by machines fitted with large spiral blades and then treated with carbon disulphide to form an orange-red sticky gelatinous mass, soluble in water, of cellulose xanthate—

$$C_6H_9O_4(ONa) + CS_2 \rightarrow C(=S)(O \cdot C_6H_9O_4)(SNa)$$

Excess carbon disulphide is distilled off under reduced pressure, and the

xanthate then dissolved in aqueous sodium hydroxide to form *viscose*. Artificial silk is produced by forcing this solution through very small holes (or spinnerets) into a bath of dilute acid, which neutralizes the alkali and decomposes the xanthate to leave a continuous filament of cellulose (or artificial silk).

Carbon Tetrachloride, CCl_4, is prepared by passing chlorine gas into boiling carbon disulphide containing a little iodine—

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$$

The carbon tetrachloride (b. p. 77°C) is separated from the sulphur monochloride (b. p. 138°C) by distillation.

Carbon tetrachloride is a relatively inert, non-inflammable liquid with excellent solvent properties for grease, etc., and is often used for this purpose in dry-cleaning of clothes, etc. It is also used in the "Pyrene" fire-extinguishers, but such fire-extinguishers must not be used to control sodium or magnesium fires, since carbon tetrachloride reacts violently with sodium vapour. Unlike other halides of the Group IV family, carbon tetrachloride is not hydrolyzed by water.

Cyanogen and its Compounds

Cyanogen, C_2N_2, may be prepared by heating mercuric cyanide—

$$Hg(CN)_2 = Hg + C_2N_2 \uparrow$$

and also by the action of potassium cyanide solution on copper sulphate solution, the cyanogen being liberated by the decomposition of the intermediate, unstable, cupric cyanide—

$$CuSO_4 + 2KCN = Cu(CN)_2 + K_2SO_4$$

$$2Cu(CN)_2 = Cu_2(CN)_2 \downarrow + C_2N_2$$

It is a colourless, poisonous gas, has a faint characteristic odour and burns in air with a peach-blossom coloured flame—

$$C_2N_2 + 2O_2 = 2CO_2 + N_2$$

It is somewhat soluble in water, with which it reacts at 0°C to form hydrocyanic and cyanic acids (HCN and HCNO)—

$$C_2N_2 + H_2O = HCN + HCNO$$

The aqueous solution on standing deposits a brown flocculent substance, known as azulmic acid. Other compounds, such as ammonium oxalate, urea and carbon dioxide, are formed at the same time. Cyanogen is absorbed by a solution of potassium hydroxide to form potassium cyanide, KCN, and potassium cyanate, KCNO—

$$2KOH + C_2N_2 = KCN + KCNO + H_2O$$

Cyanogen also combines directly with the alkali metals on heating to form the corresponding cyanides (e.g. NaCN). These reactions of cyanogen with alkali hydroxides, alkali metals, and with cold water show that cyanogen is analagous in many of its properties to the halogens, and this resemblance is further emphasized by instability of cupric cyanide and of cupric iodide which decompose to form the cuprous compound and liberate cyanogen and iodine respectively.

The formula C_2N_2 follows from its molecular weight of 52, as determined from the vapour density. The molecular structure is probably

$$N{\equiv}C{-}C{\equiv}N$$

Hydrocyanic Acid, or Prussic Acid, HCN. This very weak acid may be prepared in solution by the action of almost any acid on potassium (or other metallic) cyanide—

$$KCN + H_2SO_4 = KHSO_4 + HCN$$

The gas, hydrogen cyanide, is made by distilling the cyanide with 50 per cent sulphuric acid, and after drying by passing through a U-tube containing anhydrous calcium chloride, is condensed to a colourless liquid in a U-tube immersed in ice. It boils at 26·5°C.

Hydrogen cyanide is very soluble in water to form hydrocyanic acid (cf. hydrogen chloride which dissolves in water to form hydrochloric acid), has a characteristic odour of bitter almonds, burns in air with a purple flame and is one of the most deadly poisons known (potassium cyanide is even more poisonous due to the more potent action of the cyanide ion). Hydrocyanic acid is only a very weak acid and its salts, the cyanides, are therefore appreciably hydrolyzed by water—

$$KCN + H_2O = KOH + HCN$$

Hydrocyanic acid is used (under expert supervision) in destroying pests, for example in fumigating flour mills, ships and infested buildings. The most important cyanides are those of sodium and potassium and due to hydrolysis and the action of the carbon dioxide of the atmosphere they both smell slightly of bitter almonds. So deadly are these cyanides that death may result simply from allowing the solution to come into contact with cuts, etc. The best antidote is freshly prepared ferrous hydroxide, (prepared by adding a solution of sodium bicarbonate to one of ferrous sulphate) although quite small doses taken internally are almost immediately fatal.

Test for Cyanides. The usual method for detecting a cyanide (for example, in the sodium-fusion test for nitrogen in an organic compound) is to make the solution alkaline with sodium hydroxide, add ferrous sulphate solution and boil. If a cyanide is present, sodium ferrocyanide is formed, and this is detected by the formation of Prussian blue on

adding two or three drops of ferric chloride solution and acidifying with hydrochloric acid.

$$6NaCN + FeSO_4 = Na_4[Fe(CN)_6] + Na_2SO_4$$
$$3Na_4[Fe(CN)_6] + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 \downarrow + 12NaCl$$

Another method is to evaporate the solution to dryness on a water-bath with yellow ammonium sulphide, when a thiocyanate (e.g. KCNS) is formed. The residue is dissolved in water and added to a solution of ferric chloride to form the blood red coloration of ferric thiocyanate, $Fe(CNS)_3$.

Cyanates. Sodium and potassium cyanides are powerful reducing agents when fused. For example, they reduce many metallic oxides to the metal and at the same time are themselves oxidized to the corresponding cyanates—

$$KCN + PbO = KCNO + Pb$$

The cyanate may then be extracted by water. When the solution is acidified, cyanic acid (HCNO) is first formed, but this quickly reacts with the water to form ammonia and carbon dioxide—

$$HCNO + H_2O = NH_3 + CO_2$$

Ammonium cyanate, which played such an important part in breaking down the "vitalistic" theory of organic chemistry (*see* p. 851) is obtained on mixing concentrated solutions of ammonium chloride and potassium cyanate. When heated it undergoes an internal change (isomerizes) to form urea, $(CO(NH_2)_2$—

$$NH_4CNO \rightleftharpoons O{=}C(NH_2)_2$$

urea

FUELS AND COMBUSTION

Coal is the ultimate product of the combined effects of bacterial decay, moisture, pressure and temperature on vegetable matter (trees, leaves, etc.) which have accumulated throughout the ages. The vegetable matter slowly loses its cellulose portion and is transformed, first into peat and then into lignites, bituminous coals, and anthracitic coals, in this order. The complete conversion of vegetable matter into the final product, anthracite, may be represented by the following series—

WOOD → PEAT → BROWN LIGNITE → BLACK LIGNITE → LIGNITOUS COAL → BITUMINOUS COAL → STEAM COAL → ANTHRACITE

There is no sharp line of demarcation between these various coals, but rather a progressive change in the direction of increasing hardness and carbon content and decreasing oxygen content.

Lignite (or Brown Coal) is intermediate between peat and the bituminous coals. It usually contains over 45 per cent of volatile matter together with much moisture, and tends to disintegrate on exposure to air. Compared with other coals, it has a relatively low calorific value.

Lignitous Coal contains 40–50 per cent volatile matter and burns with a relatively long luminous flame.

Bituminous Coals are the commonest varieties. In general, they are hard and brittle and when heated produce large quantities of gas. They

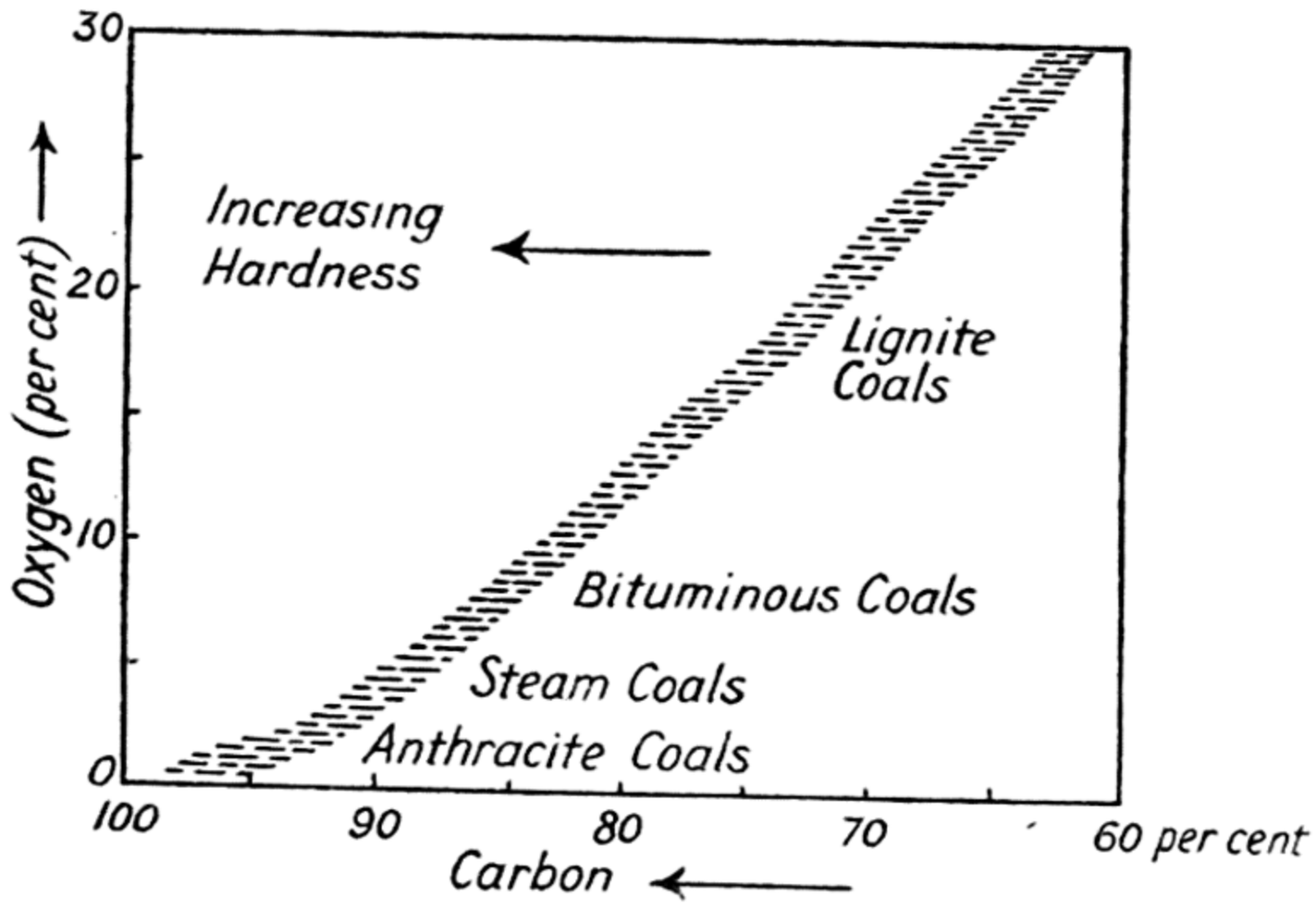


FIG. 184. Approximate Relationship between Types of Coal and their Oxygen and Carbon Content

have a typical banded appearance and consist of very bright layers (*vitrain*), laminated layers (*clarain*), dull hard layers (*durain*) and soft charcoal-like layers (*fusain*). Vitrain has a brilliant glassy lustre and breaks with a conchoidal fracture. Clarain consists mainly of minute fragments of vitrain mixed with plant debris, and has a streaky or silky appearance due to the alternation of bright, less bright, and even dull minute bands. Durain is a dull, hard coal and may occur in seams up to a foot or more in thickness to constitute the "Hards" (e.g. Barnsley Hards). Fusain is sometimes referred to as a mineral charcoal. It is only a minor constituent of most coals, and is very porous and soft.

Cannel Coal occurs in large lenticular masses in many coal seams, and appears to be related in structure to the durains. It has a greasy lustre. Some specimens ignite very easily and burn like a candle with a luminous flame, a property which accounts for its former extensive use in gas-making.

Anthracite is the hardest of the coals. It contains less than 9 per cent of volatile matter (the semi-anthracites contain from 9 to 15 per cent

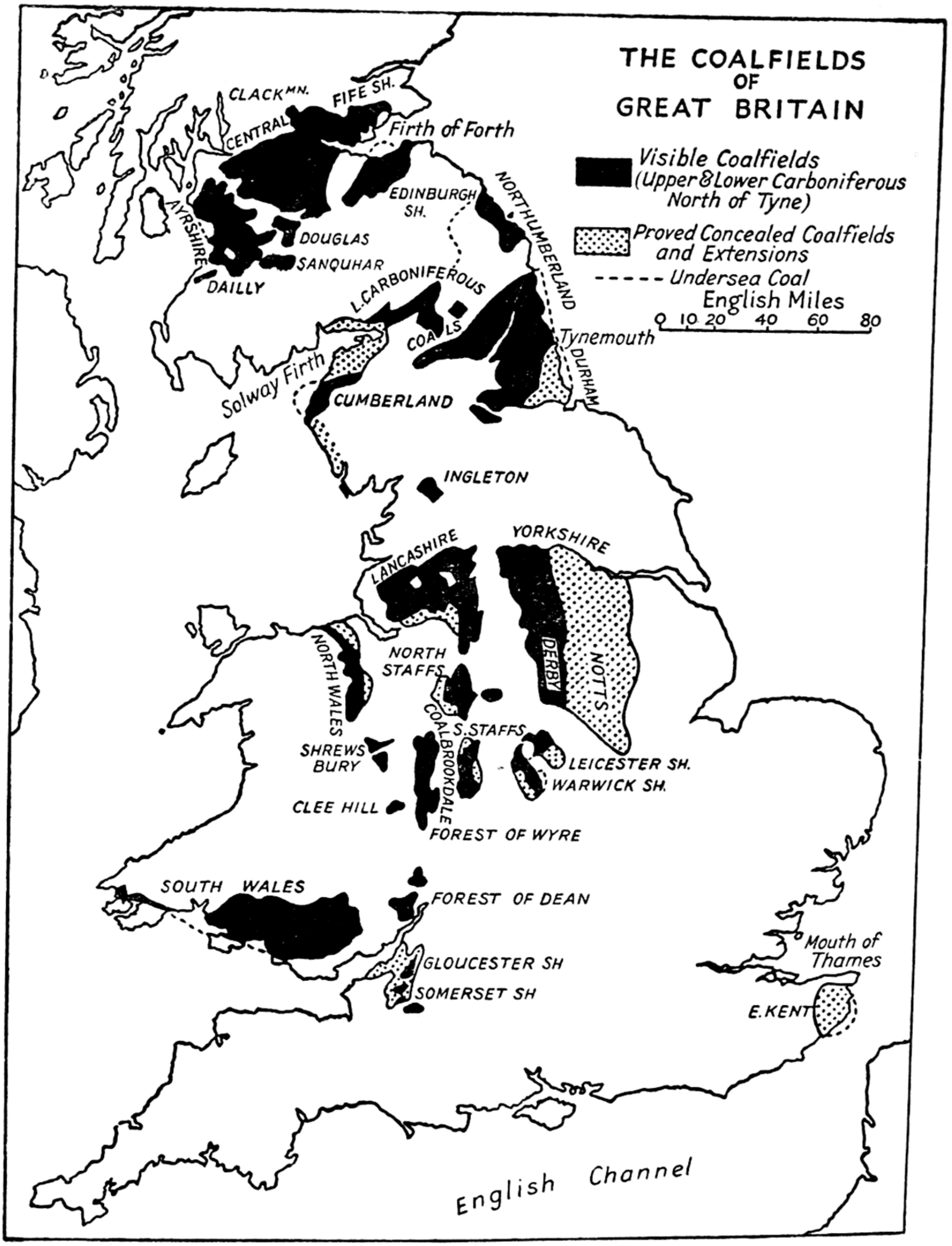


FIG. 185. Diagram of the Coalfields of Great Britain
(from Gibson's *Coal in Great Britain*)

volatile matter) and occurs as a dense, black, brittle substance, which ignites with difficulty and has a very high calorific power.

Carbonization of Coal

When a bituminous coal is gradually heated (in the absence of air) it begins to decompose between 290° and 350°C to produce various gases, such as carbon dioxide and hydrocarbons, and some liquid products, such as unsaturated and saturated hydrocarbons and phenols, etc. With increase in temperature, the evolution of hydrocarbons decreases, and above 700°C hydrogen is evolved in considerable quantities. This hydrogen results mainly from the *cracking* (or thermal decomposition) of hydrocarbons which break up into simpler hydrocarbons (saturated and unsaturated), hydrogen and carbon. For example—

$$C_3H_8 \rightarrow C_2H_4 + CH_4$$
$$CH_4 \rightarrow C + 2H_2$$

The carbon is graphitic in character and is deposited on the walls of the retorts as the very hard *gas-carbon*, and also in the pores of the coke residue to give the latter a grey appearance. Coke carbonized at lower temperatures is not coated with this graphite deposit, and in general is more easily ignitible.

Coal is a bad conductor of heat. With an external carbonizing temperature of about 1000°C, the temperature at the centre of a column of coal twelve inches thick after several hours may not be much more than 100°C. This poor conduction of heat is aggravated by the various changes which the coal undergoes in its conversion to coke. In the initial stages it becomes plastic, and then more and more viscous, until it eventually becomes the rigid coke. A zone of plastic coal thus gradually moves away from the surface towards the centre of the coal mass and this plastic zone acts as a heat barrier and retards the supply of heat to the centre. As a result, even with an external carbonization temperature of about 1000°C, the rate of coking may only be about 0·8 in. per hour.

The liberation of gases during the plastic stage tends to blow the "liquid" coal into a froth, and if the coal is free to expand at this stage a swollen open-textured coke is obtained. If, however, this expansion is resisted by the type of plant employed, a dense coke with a fine-pore structure is obtained instead.

The heterogeneous nature of the products obtained by the carbonization of coal is mainly the result of the practical impossibility of heating the whole mass of the coal to the same uniform temperature, whether this be high (> 1000°C) or low (c 600°C). Even when the carbonization is carried out in retorts at 1000°C or higher, many of the products associated with the lower temperature process must also be present because of the much lower temperature which obtains in the centre of the coal mass. In

general, however, it may be said that increase in temperature of carbonization increases the volume of gas and decreases the proportion of coke and tar products. The higher the temperature, the greater the proportion of hydrogen in the coal gas; the lower the temperature, the greater the proportion of hydrocarbons in the coal gas. Thus carbonization at low temperatures produces a luminous gas, whilst carbonization at high temperatures produces a relatively non-luminous gas.

TABLE 91

Typical Variation of Yield with Temperature

Carbonization Temp. °C	500	600	700	800	900	950
Coke (per cent) .	85·3	75·4	70·1	67·7	66·4	68·6
Tar (per cent) . .	4·5	7·7	7·7	7·7	7·7	5·0
Gas (per cent) . .	3·4	7·7	10·5	12·2	13·4	19·4

Manufacture of Coal Gas. Coal gas was first introduced as an illuminant by Murdoch in 1792, and was first used for public lighting in 1802. The use of iron retorts in the early days of the industry meant that carbonization could not be carried out at a temperature much higher than about 700°C. This resulted in a readily combustible (non-graphitic) coke and a relatively low yield of coal gas with a high illuminating power (due to its high hydrocarbon content). The invention of the Bunsen burner in 1855, and the later development by Welsbach of the incandescent gas-mantle

TABLE 92

Typical Analysis of Coal Gas as a Function of Carbonization Temperature

(*after Gyngell*)

Carbonization Temp. °C	CO	C_2H_6	CH_4	Coal H_2	Total Gas
	ml/g of coal				ml/g
600	7	19	35	25	86
700	10	17	42	40	109
800	25	12	58	105	200
900	36	17	48	150	251
1000	46	11	52	170	279

containing certain metallic oxides (CeO_2 and ThO_2) which become highly incandescent on heating, reduced the need for a gas of high illuminating power. The iron retorts were provided with silica linings or were replaced entirely by refractory retorts, and the temperature of carbonization increased, so that nowadays temperatures of more than 1000°C are usual.

The products of the carbonization of coal fall naturally into four groups—

$$\text{Coal} \rightarrow \begin{cases} \text{Coal gas} \\ \text{Ammoniacal liquor} \\ \text{Coal tar} \\ \text{Coke (and gas carbon)} \end{cases}$$

Coal gas is composed principally of hydrogen, methane (CH_4), and carbon monoxide, and after purification may have the following approximate composition—

TABLE 93

Percentage Composition by Volume of Coal Gas

Gas	Percentage
Hydrogen	56
Methane	23
Other hydrocarbons	3
Carbon monoxide	10
Carbon dioxide	2
Nitrogen	5
Oxygen	1

Ammoniacal Liquor. This contains ammonia, ammonium carbonate, ammonium chloride, ammonium sulphide, phenol, pyridines, and small quantities of certain other organic compounds.

Coal Tar is particularly valuable, and is the source of various hydrocarbons, such as benzene ("benzole"), toluene, naphthalene, from which are manufactured a host of substances, such as the coal-tar dyes, plastics, drugs, etc.

The coal is carbonized at about 1000°C in either horizontal or vertical retorts heated by producer gas. In the horizontal type, some 12–14 cwt of coal in a layer 12 in. thick are carbonized at rest in about 8 to 12 hours. In the vertical type, there is the intermittent process in which the charge of about $2\frac{1}{2}$ tons of coal is carbonized at rest in about 12 hours, and also the continuous process in which the coal is fed in, more or less continuously, at the top and the resulting coke continuously withdrawn at the bottom

of the retort. Depending upon the size of the retort and the type of coal used, the latter process may carbonize from 3 to 12 tons of coal a day.

Horizontal Retort Process. This is the oldest, but still one of the most important, of the present-day processes. Each retort consists of an elongated shallow chamber of fire-clay or silica (20 ft long by 16 in. wide by 13 in. high approx.) bee-hive shaped (⌒) in vertical cross-section, and fitted at each end with cast-iron doors and ascension pipes for conveying the volatile products, through a water-seal, to the hydraulic main. A number of such horizontal retorts are arranged in tiers and heated externally by the combustion of producer gas, generated in a furnace immediately below the retorts. These furnaces are fed with hot coke pushed direct from the retorts. When carbonization is complete (8–12 hr), the retorts are opened and horizontal rams used to push out the red hot coke which is then quenched by water.

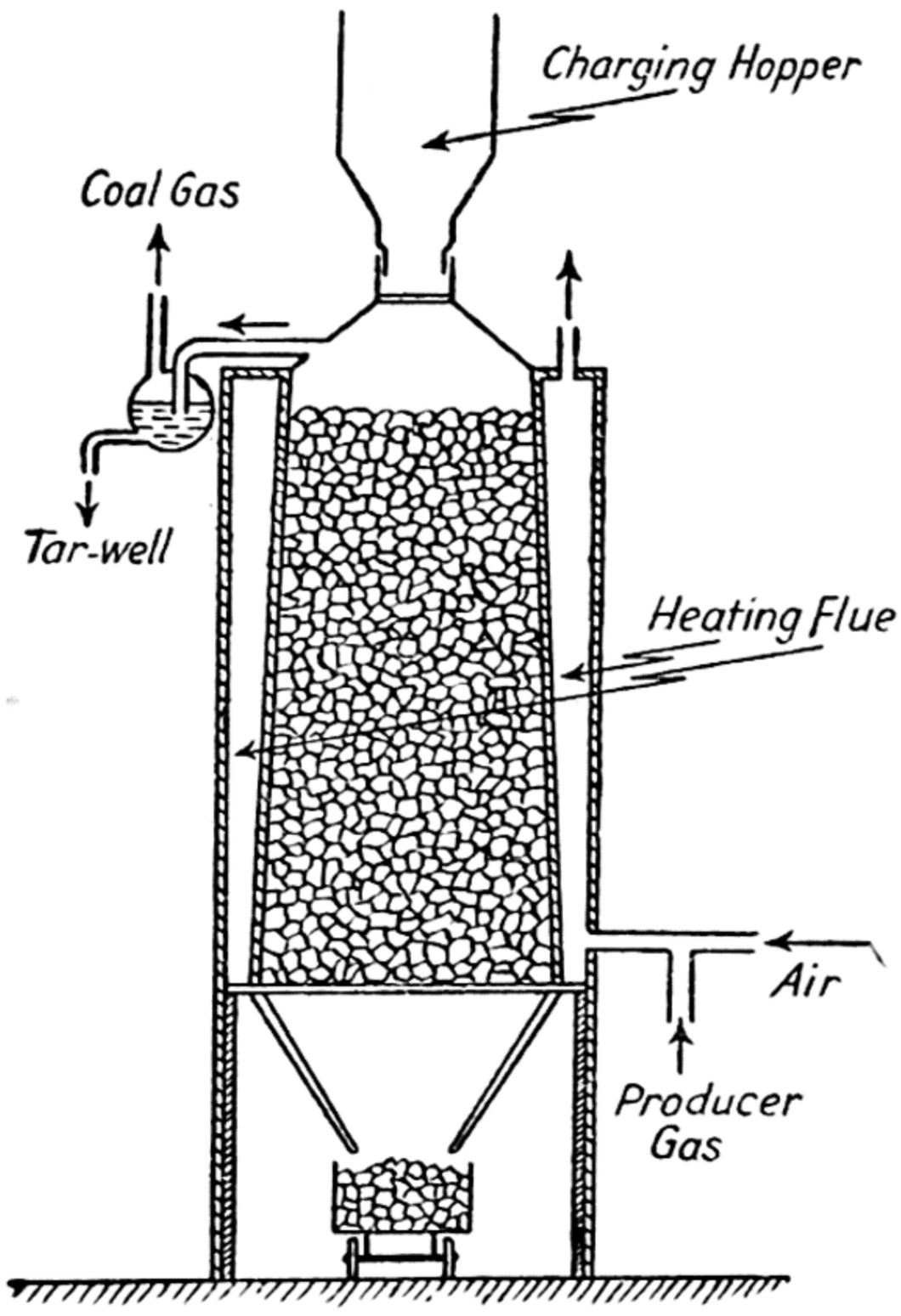


FIG. 186. Intermittent Vertical Retort

Intermittent Vertical Retort Process. This is the most modern process and uses an elongated rectangular oven of mean dimensions 16 ft high by $9\frac{1}{2}$ ft long by 11 in. wide broadening towards the base. A number of such units are grouped vertically together and, as in the horizontal process, these are heated externally by the combustion of a mixture of producer gas and air in flues arranged vertically between the units. Coal is charged in from the top, and at the end of the carbonization period the coke is discharged directly, via hoppers, to trucks, etc. Steam is usually admitted at the base of the retort for the last two hours of the carbonization period, and serves both to quench the coke and to increase the gas yield by the water-gas reaction.

Continuous Vertical Retort Process. This process uses a number of retorts which are either rectangular or oval in horizontal cross-section and about 25 ft in height. The coal is fed in through hoppers at the top, and the retorts heated by producer gas burning in horizontal or vertical flues. Steam is blown continuously into the base of each retort, and, as above, serves to quench the issuing coke and also to increase the gas yield.

The coal gas and other volatile products (tar, water, etc.) pass from

the retorts via a water seal to the hydraulic main, and from there to the condensers, which consist of a long continuous series of iron pipes through which the gas must pass. Some of the less volatile materials condense in the hydraulic main, but the bulk of these compounds condense in these iron pipes. The condensate from the hydraulic main and from the condensers is run off to the tar-well, where it separates into an upper aqueous

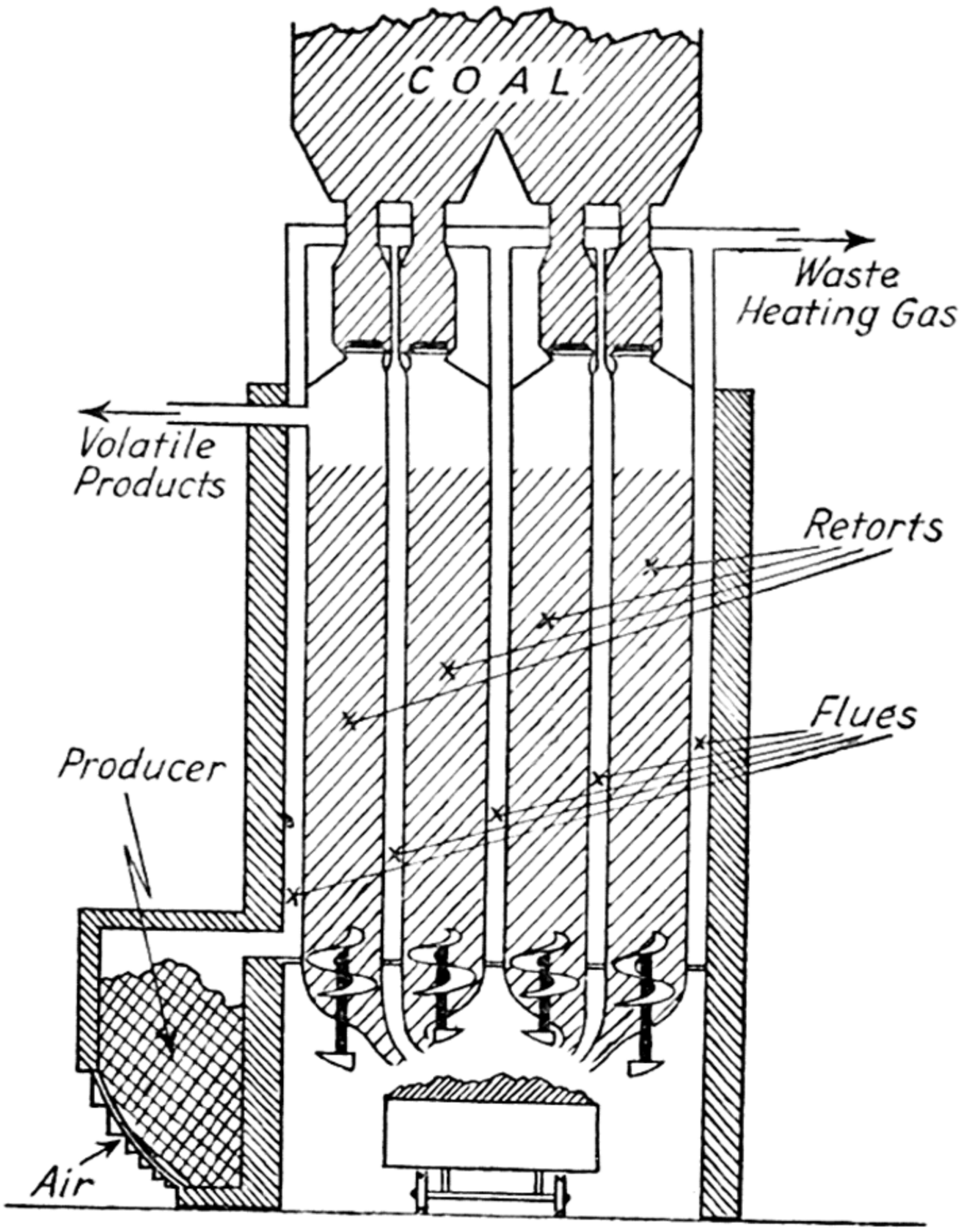


FIG. 187. Continuous Vertical Retort

layer and into a lower tar layer. Last traces of tar-fog are removed from the gas either by electrostatic precipitation or by a Livesey washer containing ammoniacal liquor. The coal gas then passes to the scrubbers, which consist of towers filled with spray-distribution boards in which the ascending coal gas meets a descending spray of water. The remaining ammonia and some of the sulphuretted hydrogen and carbon dioxide are removed in this treatment. The gas then has to be purified from residual sulphur compounds (sulphuretted hydrogen, carbon disulphide, etc.) before passing through the gas-meter to the gas holder (note: *not* the "gasometer"). In practice, the calorific value of the coal gas is controlled by the addition of water gas.

Purification. The coal gas is passed through beds of hydrated iron oxide (bog iron-ore) where the sulphuretted hydrogen is absorbed in the formation of ferric sulphide by the following possible reaction—

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$$

By the regulated introduction of about 2 per cent of air into the gas at this stage, together with a trace of ammonia, and with temperature control, this sulphide is continuously reoxidized to iron oxide and free sulphur. The oxide begins to lose its efficiency when it contains about 55 per cent of free sulphur, and is then used to manufacture sulphuric acid (usually, by the lead-chamber process). This acid is then used to convert the ammonia present in the ammoniacal liquor into ammonium sulphate (or "sulphate of ammonia").

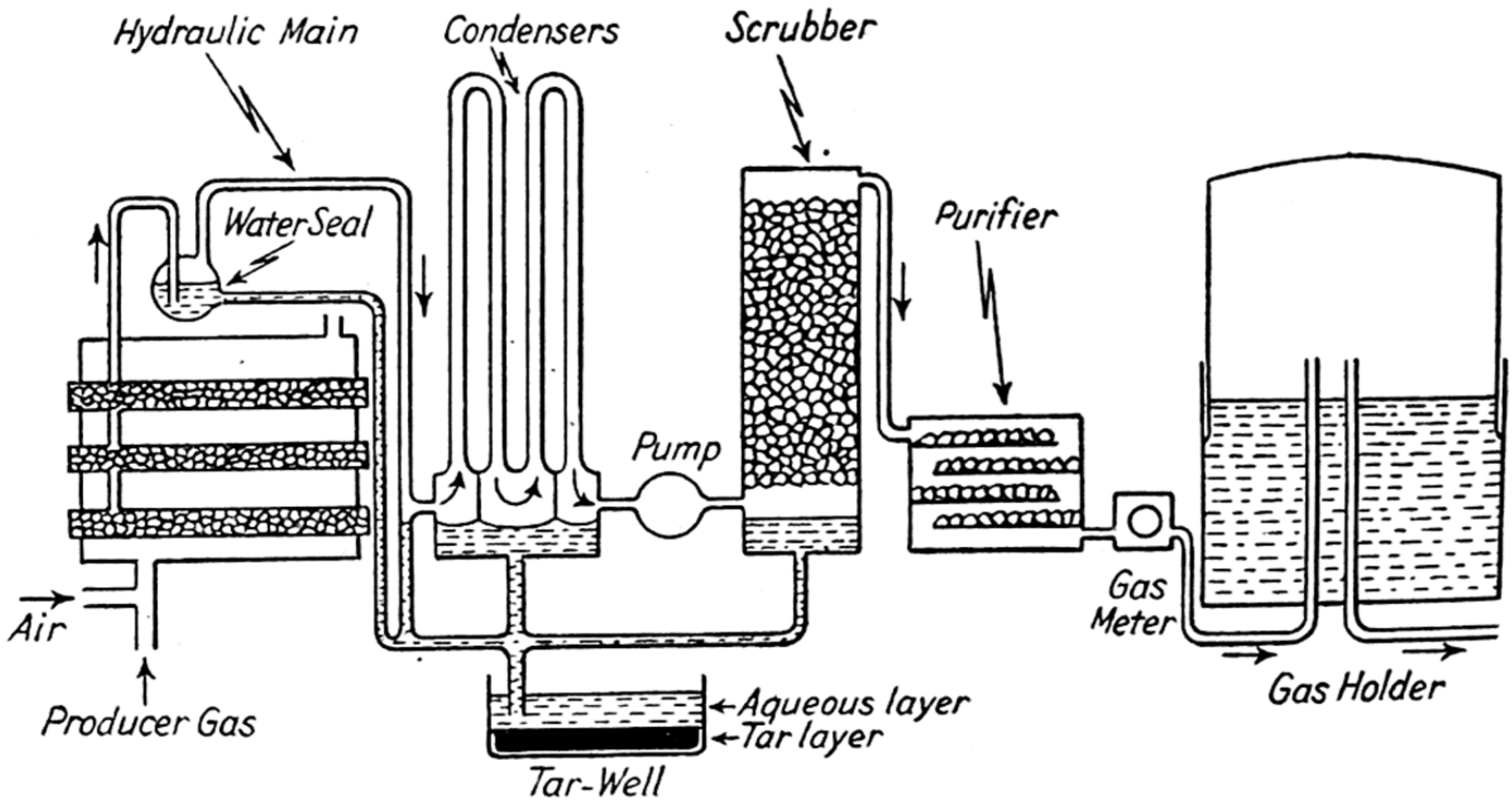


FIG. 188. Manufacture of Coal Gas

Carbon disulphide is removed by passing the coal gas over a nickel catalyst at about 450°C, when the following reaction occurs—

$$CS_2 + 2H_2 = 2H_2S + C$$

The sulphuretted hydrogen is then removed as above by hydrated ferric oxide. The carbon deposit, which interferes with the activity of the nickel, is periodically (approximately once a month) burnt to carbon dioxide by drawing air through the heated catalyst chamber.

The coal gas is then *stripped* of benzole and naphthalene before it is metered and passed into the gas-holders. The benzole is removed either by oil scrubbing, or by activated charcoal. In the first of these processes, the benzole is dissolved in creosote oils or petroleum oils in large towers, about 70 ft high, which ensure intimate contact between the gas and the

oils. The benzoles (toluene, etc.) are then recovered by distillation, and the oils returned to the top of the towers. In the activated charcoal process, the benzole is adsorbed on charcoal. The latter takes up about 30 per cent of its weight of benzole, which is subsequently recovered by treatment with steam, and the charcoal used again.

Manufacture of Coke. Apart from the coke obtained as a by-product in the manufacture of coal gas, considerable quantities of coke with special properties are required for many metallurgical operations (for example, in the manufacture of pig-iron in the blast-furnace). These cokes are usually produced in coke-ovens under conditions which vary with the type of coal used and the particular demands of the industry in which the coke is to be used. In these processes, coal gas, coal tar, etc., are regarded as by-products.

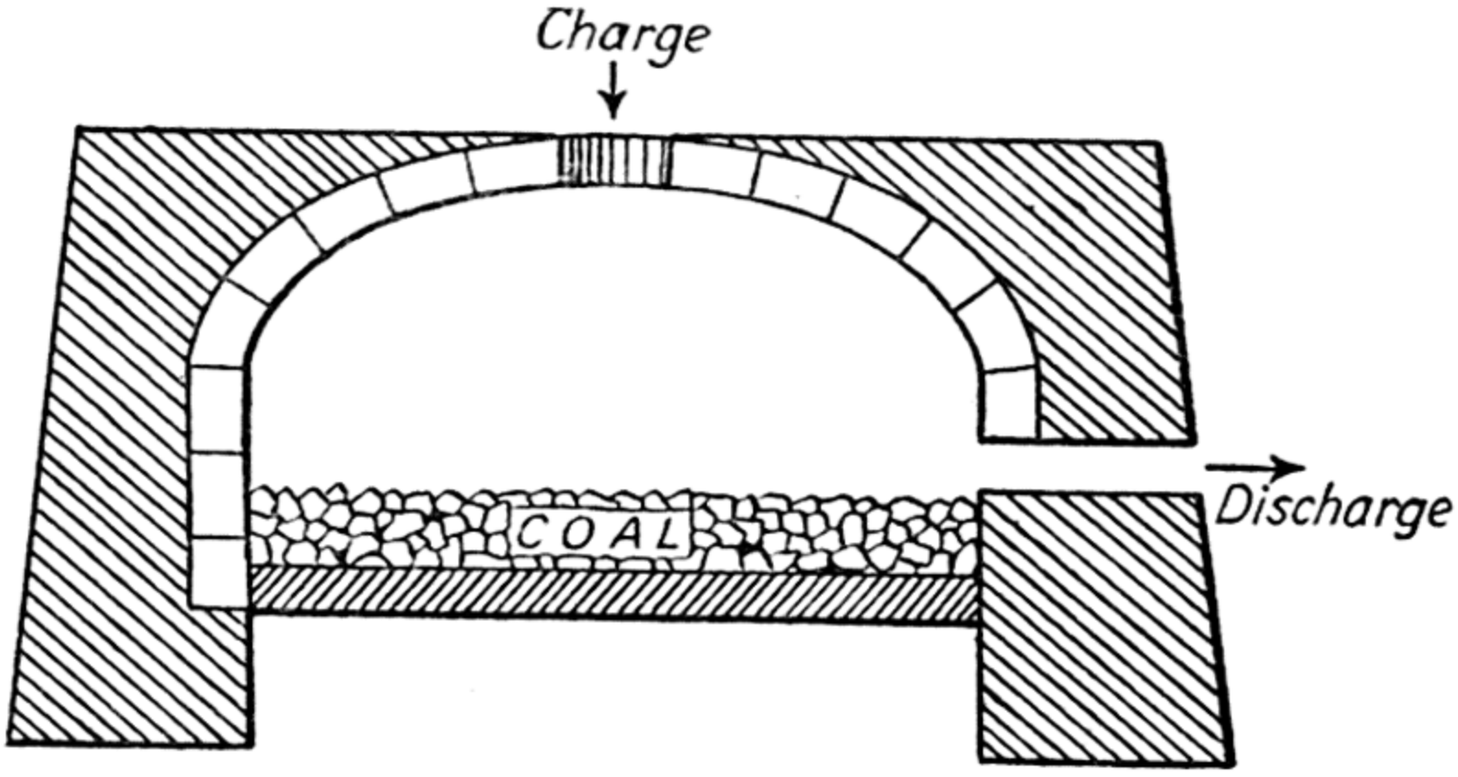


FIG. 189. Beehive Coke Oven

Bee-hive Ovens. The earliest metallurgical cokes were produced in the now obsolescent bee-hive oven, shown in the accompanying diagram. Coal was charged into the hot oven through a hole in the roof and formed a layer up to two feet thick. The volatile matter was burnt inside the chamber by air admitted through the partially bricked up door, and provided the heat for the carbonization of the coal. When carbonization was complete, the coke was quenched with water and raked out, leaving the furnace hot enough to start the carbonization of the next charge.

Modern Coke-ovens. These differ from the bee-hive ovens in being heated externally either by a portion of the coal gas produced during the carbonization of the coal or by blast-furnace gas or by producer gas. The ovens, which are constructed of silica brick and consist of narrow rectangular chambers each 40 ft long, 12–14 ft deep, and 14–18 in. wide, are erected side by side with vertical flues between them to form a battery. Each chamber is provided with the usual gas off-takes, with four charging holes at the top and with refractory lined cast-steel doors at each end. After carbonization, the coke is discharged horizontally by a massive ram. In effect, the ram pushes a more or less solid wall of coke from the

chamber into a large quencher car and thence to a central quenching station. Modern ovens hold about 14 tons of coal which is carbonized in about 8 hours at a flue temperature of approximately 1300°C.

Usually a strong swelling coal is used, and as these are not free to expand during the plastic stage (*see* p. 585) a strong dense coke results. Also, since the carbonization occurs at very high temperatures, considerable cracking of the various hydrocarbons occurs with deposition of carbon in

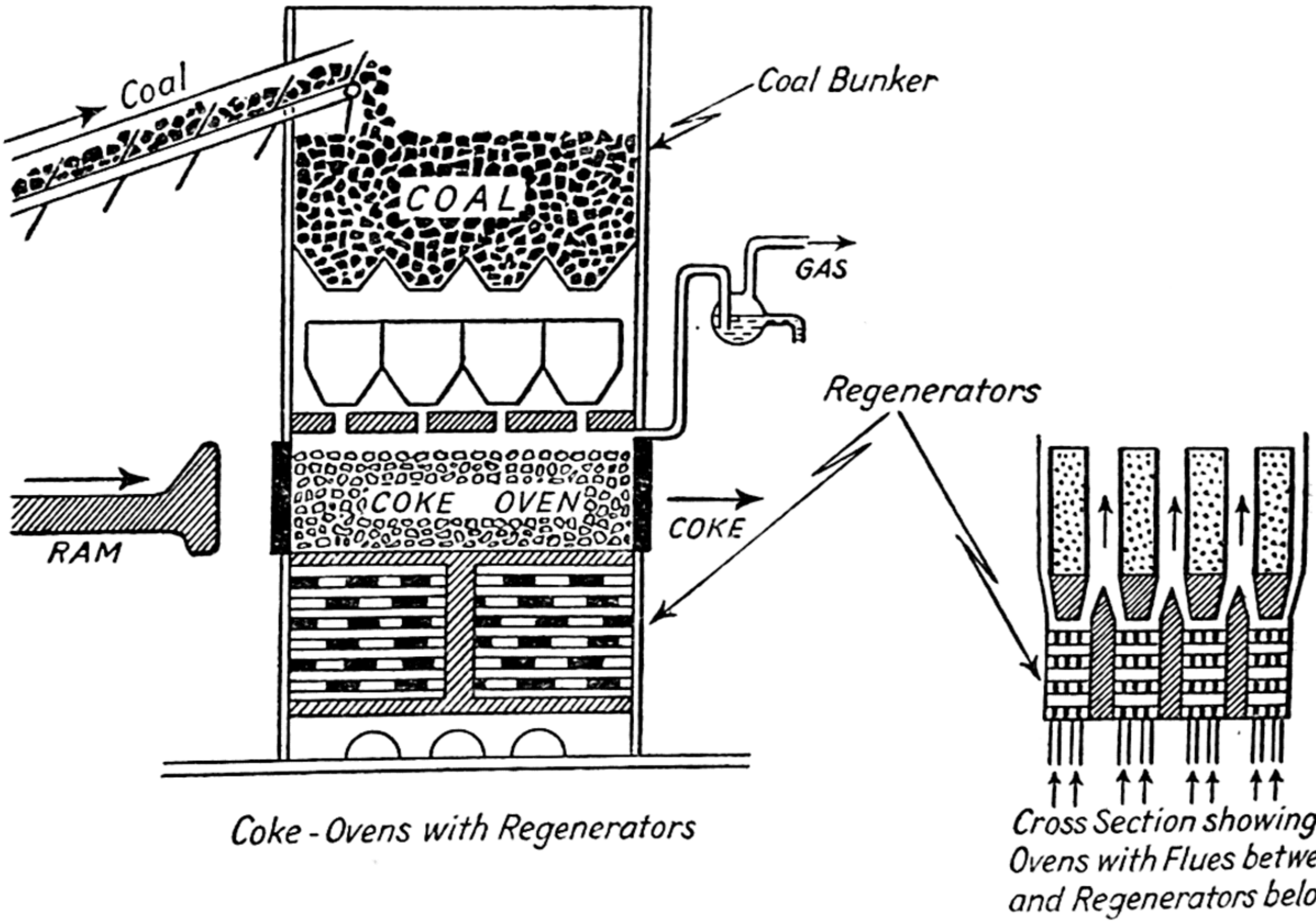


FIG. 190. Modern By-product Coke Oven

the form of graphite in the pores of the coke, so that in addition to being relatively hard the coke is also of the non-reactive type. Of the 13 000 000 tons of coke produced in this way in coke-ovens each year, 90 per cent is consumed in blast furnaces in the manufacture of pig-iron, and most of the remainder in converting this pig-iron into steels.

Low Temperature Carbonization. A development of recent years is the process whereby coal is carbonized at low temperatures (600°C) to produce a smokeless fuel. The chief difficulty is to ensure sufficiently rapid carbonization of the coal without over-carbonizing the outer layers as in the usual coke-oven and coal gas practice. This difficulty is surmounted, for example, in the Parker process (as used by Low Temperature Carbonization Ltd.), by carbonization in thin layers by external heating, but other methods are also used.

In the Parker process, the coal is carbonized in long, small-bore, vertical retorts, tapering from $4\frac{1}{2}$ in. at the top to $5\frac{1}{2}$ in. at the base. Twelve such retorts are formed as tubular holes in a cast-iron block, 9 ft high and 4 ft across the base. Each block is fitted with a common gas off-take and coal-charging hopper. A battery consisting of 36 such multi-tubular retorts is heated externally by producer gas, by radiation rather than by direct flame. Each tube holds about 50 lb of coal and acts as an intermittent vertical retort, the carbonization period lasting for about four hours.

The average yield of the various products obtained by this process, per ton of coal carbonized, is—

Smokeless fuel	14 cwt
Crude coal oil (tar)	18 gal
Crude petrol	3 gal
Gas	4000–5000 ft^3
Ammonium sulphate	4 lb
Aqueous liquor	20 gal

Compared with the high temperature carbonization processes, low temperature carbonization results in the production of—

(*a*) A smokeless, easily ignitible, solid fuel, which is sold for industrial and increasingly for domestic use under the name "Coalite."

(*b*) Petrols (i.e. aliphatic hydrocarbons) as well as some of the benzoles (aromatic hydrocarbons) of the high temperature process.

(*c*) Increased yields of tar (18–20 gal per ton of coal as compared with 9–10 gal). These tars are rich in phenols.

Hydrogenation of Coal. The hydrogenation of coal to produce petrol is a comparatively recent process. It is successfully carried out on a large scale in this country by Imperial Chemical Industries at their Billingham plant. The cleaned coal is first ground and mixed with heavy oil (recovered from a later stage in the process) to form a paste containing 50 per cent coal and 50 per cent oil. This paste is then pumped continuously, together with hydrogen at about 250 atmospheres pressure, through heat exchangers and preheaters to the reaction vessel which is maintained at 450°C. The reaction vessel contains as catalyst an organic compound of tin and hydrochloric acid which is kept stirred by the passage of hydrogen gas through it. From the reaction vessel, the issuing gases pass, via the scrubber, to the condensers where the liquid fraction is condensed. The liquid fraction is collected and separated by distillation to produce a petrol fraction, a middle oil fraction and a heavy oil fraction. The latter is used partly in producing the initial coal-oil paste, and the remainder is hydrogenated further to produce more petrol. The middle-oil fraction is also hydrogenated again, and this is effected by vaporizing the oil and passing the vapour and oil through the catalyst chamber. The uncondensed

gases from all these processes are further scrubbed and are then passed to the hydrogen plant as a source of more hydrogen.

In addition to coal, considerable quantities of low-temperature tar and creosote oils are also hydrogenated in this way at the Billingham plant. Working at capacity, the plant was designed to produce some 150 000 tons (45 million gallons) of petrol per annum, made up of 100 000 tons from coal, 40 000 tons from creosote and 10 000 tons from low-temperature tar. For every ton of coal converted completely into petrol, about three tons of coal are required for such purposes as manufacturing and compressing the hydrogen and supplying power to the plant.

Gaseous Fuels

Coal Gas. An analysis of coal gas has already been given on p. 586.

Producer Gas is essentially a mixture of nitrogen and carbon monoxide obtained by blowing air through a bed of carbon at 1000°–1200°C. Presumably the oxygen of the air is first converted into carbon dioxide which is then reduced to carbon monoxide as it passes upwards through the hot coke—

$$C + O_2 = CO_2 + 94\,450 \text{ cal.}$$

$$CO_2 + C = 2CO - 41\,200 \text{ cal.}$$

The proportion of carbon monoxide and carbon dioxide in the issuing gas is however determined by the temperature of the coke. The second reaction is very strongly endothermic so that increase in temperature, by Le Chatelier's principle, leads to an increase in the equilibrum concentration of the carbon monoxide, as indicated by the following figures—

Temperature °C	Percentage of CO	Percentage of CO_2
450	2·0	98·0
750	76·0	24·0
1050	99·6	0·4

Even when the main part of the producer is working at 1000°C, however, there is a small tendency for some carbon monoxide produced in the hotter zones to revert to carbon dioxide in the cooler upper zone, so that producer gas usually contains a small proportion of carbon dioxide. With this reservation, producer gas may be said to consist of about 34 per cent of carbon monoxide and 64 per cent of nitrogen by volume.

Since producer gas is nearly two-thirds nitrogen it is not economical to manufacture it in one locality and then use it elsewhere. Instead, it is normally made in situ, a practice which also enables the additional heat

which the gas possesses, by virtue of its high temperature as it leaves the producer, to be utilized straight away.

Semi-water Gas. The overall reaction involved in making producer gas is highly exothermic, so that the temperature of the coke rises and this increase in temperature sometimes leads to difficulties due to clinker or slag formation. In the production of water gas, on the other hand (*see* below), the reactions involved are strongly endothermic and the coke is rapidly cooled below the operating temperature. By admitting steam and air simultaneously into the hot producer, the heat evolved by the producer gas reactions can be balanced by the heat absorbed by the water gas reaction, and the temperature of the coke bed can also be adjusted by

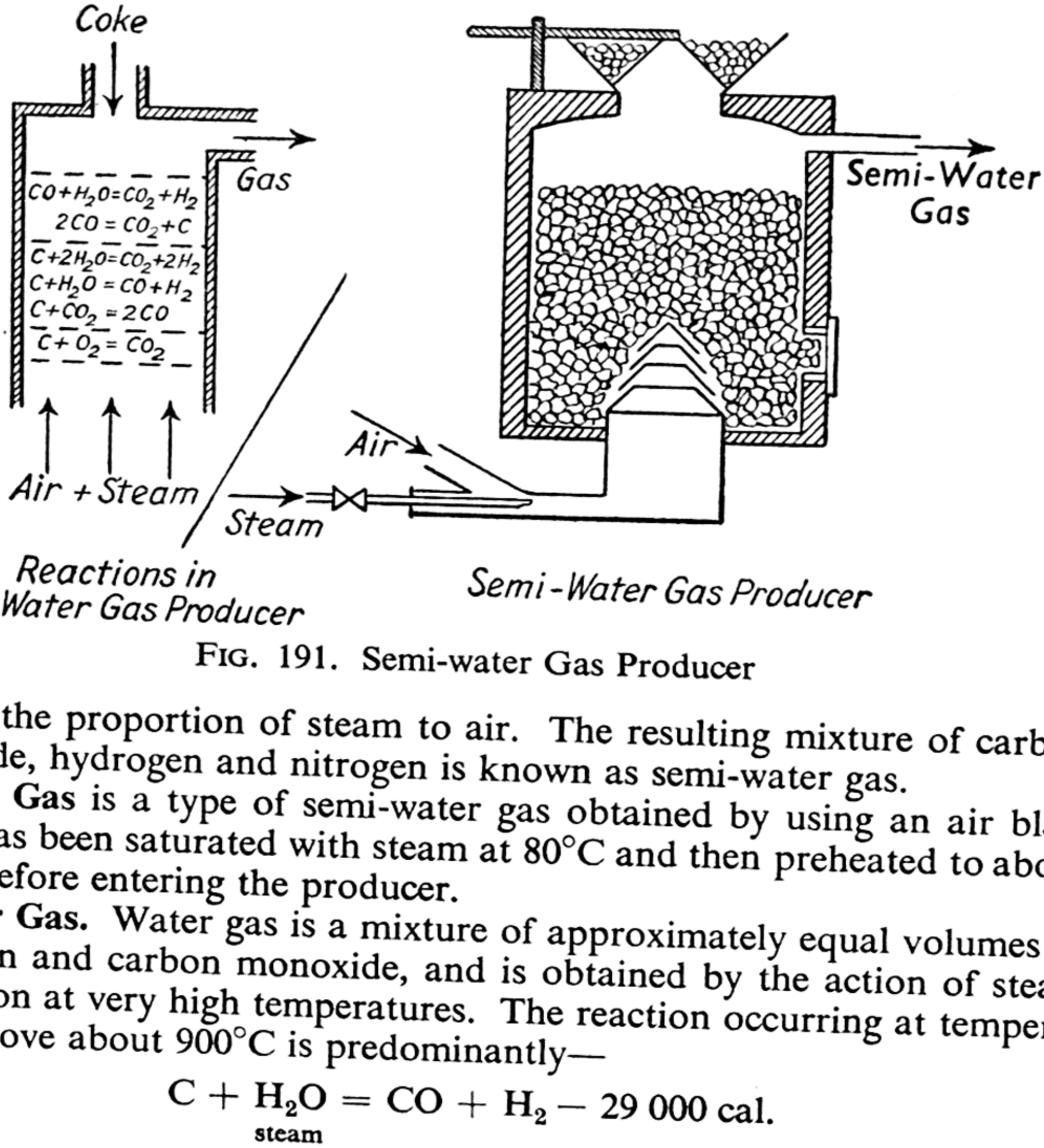


FIG. 191. Semi-water Gas Producer

varying the proportion of steam to air. The resulting mixture of carbon monoxide, hydrogen and nitrogen is known as semi-water gas.

Mond Gas is a type of semi-water gas obtained by using an air blast which has been saturated with steam at 80°C and then preheated to about 250°C before entering the producer.

Water Gas. Water gas is a mixture of approximately equal volumes of hydrogen and carbon monoxide, and is obtained by the action of steam on carbon at very high temperatures. The reaction occurring at temperatures above about 900°C is predominantly—

$$C + \underset{\text{steam}}{H_2O} = CO + H_2 - 29\,000 \text{ cal.}$$

but at lower temperatures increasing quantities of carbon dioxide are produced by the reaction—

$$C + \underset{\text{steam}}{2H_2O} = CO_2 + 2H_2 - 19\,000 \text{ cal.}$$

The almost complete absence of carbon dioxide at high temperatures is most simply explained by the endothermic nature of the reaction—

$$CO_2 + C = 2CO - 41\,200 \text{ cal.}$$

although the hydrogen probably plays some part in this reduction.

The endothermic nature of these reactions results in a rapid cooling of the coke with increasing production of the non-combustible carbon dioxide until the reaction eventually ceases.

The only practical way in which the coke-bed can be maintained at about 1000°C is to alternate the water-gas "run" with a producer gas "blow." The coke is first raised to about 1200° to 1400°C by an air-blast (the blow), the air-blast is then shut off and the steam-blast turned on (the run). This latter run stage lasts only for a few minutes to be followed by a fresh blow, and so on. In some plants, two generators are blown in parallel and then run in series, a practice which is equivalent to using a shallow fuel bed for the blow and a deep bed for the run periods. The time of the blow period is thereby reduced and the time of the run period increased. Water gas is often known as *blue water gas* to distinguish it from carburetted water gas described below.

Carburetted Water Gas. Water gas is often added to coal gas as a convenient and quick method for increasing the supply of available gas. Since, however, water gas has a lower calorific value than coal gas, it is desirable that it be enriched in some way so as to increase its calorific value. This is effected by utilizing the heat of the producer gas formed during the blow to crack various oils. The gas generated during the blow is allowed to burn in chequer brickwork chambers known as the carburettor and the superheater, thereby raising the temperature of these chambers to between 700° to 1000°C. During the succeeding run, a fine spray of petroleum oils, or less frequently creosote oils, is injected into the carburettor where it vaporizes and mixes with the water gas. In the superheater, this oil is cracked by the high temperature to form various gaseous hydrocarbons (methane and some unsaturated hydrocarbons) and hydrogen, which mix with the blue water gas to form carburetted water gas.

Combustion and Flame

Combustion in its widest sense implies chemical reaction between two substances, of which one at least is gaseous, with the liberation of heat. Thus, we speak of the burning of various substances, such as coal, paraffin or hydrogen in air, as combustion. Such reactions might be, and indeed usually are, referred to as oxidations since one of the reacting substances is oxygen. Combustion may, however, occur with other gases besides oxygen. Thus magnesium will burn in steam and also in nitrogen; antimony and phosphorus will burn in chlorine; and so on.

All these reactions occur with liberation of heat, and it is this heat

liberation which determines whether combustion occurs or not. The heat liberated must be sufficient to make the reaction self supporting once it has been started. Mercury will combine with oxygen on heating, but we do not call this reaction combustion because the reaction ceases as soon as the external heat supply is cut off; the heat liberated is insufficient to maintain the temperature required for the reaction to occur by itself.

Combustion may or may not occur with emission of light. The slow combustion which occurs in the very slow process of decay of animal and vegetable matter, the slightly quicker combustion which makes all forms of life possible, and the rusting of metals are all forms of oxidation which occur with evolution of heat with no emission of light. Rapid combustions, such as occur when benzene is burnt in air, or more violent combustions, such as occur in many gaseous explosions, are accompanied by the rapid evolution of heat and emission of light. The final products and the total amount of heat liberated may be the same in two extreme cases, but the rate at which the heat is liberated will vary from almost infinitesimally slow in the case of decay to extremely rapid in the case of the explosion, and it is this rate of heat evolution which determines whether or not emission of light occurs.

Flame is only produced by the combustion of a gas or vapour; it implies that reaction is occurring in the gaseous phase with sufficient evolution of heat energy for some to be transformed directly into light energy, or to be absorbed by any minute solid particles present so that these become incandescent. When a solid burns with evolution of flame it indicates either that the heat liberated is sufficient to convert some of the solid into vapour (which then produces the flame) or else that the oxidation of the solid produces an intermediate inflammable gas (which in its turn burns to produce flame). Volatile solids such as phosphorus, sulphur, stearic acid, etc., burn with flame because the reaction occurs between their vapour and air. Metals like magnesium and zinc will also burn with flame if they are heated sufficiently strongly to volatilize some of the metal and initiate combustion. The heat of the combustion then provides the necessary heat for the progressive volatilization and continued combustion of the remainder of the metal. The flame may result partly from the emission of some of the heat as light energy, and partly from raising the temperature of the minute solid particles (MgO, ZnO) produced during the combustion to incandescence. Silicon and iron on the other hand are not easily vaporized; the combustion here occurs between the solid iron and oxygen. The heat liberated is sufficient however to raise the temperature of the silicon and iron so that they become incandescent and burn with a brilliant flameless light. Carbon, which can only be volatilized above about 3000°C, similarly will burn without producing flame. The blue flame frequently seen when carbon burns is due, not to the carbon, but

to the formation of carbon monoxide gas as an intermediate volatile inflammable product.

SILICON

Occurrence. Silicon is second only to oxygen in its abundance in nature, but it does not occur in the free state. It occurs principally as its oxide, silica, and also in many oxy-compounds based on this oxide, such as the silicates which form the major constituent of the earth's crust. The naturally occurring forms of silica, SiO_2, include quartz, sand, flint, agate and kieselguhr. Examples of the large number of silicates found in nature include the felspars, clays, micas, zeolites, amphiboles and pyroxenes, the structures of which are discussed later in this chapter.

Preparation of Silicon. Silicon, like boron, has a high affinity for oxygen so that powerful methods are necessary to obtain the element from its compounds. The chief methods are as follows—

(*a*) *Reaction with elements which have a higher affinity for oxygen.* Silicon may be prepared by heating a mixture of silica and magnesium powder—

$$SiO + 2Mg = Si + 2MgO$$

The magnesium oxide (and magnesium silicide which forms at the same time) is then separated by treatment with dilute hydrochloric acid, to leave the silicon as a dark-brown amorphous powder.

(*b*) *From halogen compounds of silicon.* Silicon is also obtained when metallic sodium or potassium is heated in an atmosphere of silicon tetrafluoride (or tetrachloride), or when a mixture of potassium fluosilicate and potassium is strongly heated—

$$SiF_4 + 4Na = Si + 4NaF$$

$$K_2SiF_6 + 4K = Si + 6KF$$

(*c*) *Commercially*, silicon is prepared at Niagara Falls and elsewhere by heating crushed coke with excess of sand in an electric furnace. If excess of sand is not used, the principal product is carboundum, that is, silicon carbide.

$$SiO_2 + 2C = Si + 2CO\uparrow$$

The reaction occurs more or less completely from left to right because the oxygen is removed as the gas, carbon monoxide, but even so, very high temperatures are necessary.

(*d*) *A crystalline form of silicon* is made by preparing silicon in the presence of excess of aluminium or zinc. The resulting solution of silicon in these molten metals deposits needle-shaped crystals of silicon on cooling. The aluminium or zinc is then removed by treatment with dilute hydrochloric acid.

Properties of Silicon. As normally prepared, silicon is a dark-brown

amorphous powder, with a density of about 2·35. It melts at about 1500°C and may be vaporized at the temperature of an electric arc. Crystalline silica is a dark-grey substance with a metallic lustre, and is hard enough to scratch glass. Its density is variable, depending on how it is prepared, but approximates to 2·5, and it differs from amorphous silicon in its ability to conduct electricity. It is also slightly less reactive chemically.

Silicon oxidizes superficially when heated in air, but will burn when heated in chlorine, and ignites spontaneously in fluorine (a property shared also by its compounds, such as the silicates). The element is insoluble in water and in acids, with the exception of hydrofluoric acid which dissolves it to form hydrofluosilicic acid, H_2SiF_6—

$$Si + 6HF = H_2SiF_6 + 2H_2 \uparrow$$

Silicon will also dissolve in boiling aqueous alkalis to form a solution of the alkali silicate and liberate hydrogen—

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2 \uparrow$$

Silicon will react with many metals to form silicides (for example, ferro-silicon, FeSi, and magnesium silicide, Mg_2Si), and its carbide SiC is familiar under the name "Carborundum."

Uses of Silicon. The element has very little use by itself, but it forms an important constituent of many alloys, to which it imparts hardness (e.g. silicon-bronze) and resistance to acids (e.g. a silicon-iron alloy). Its compounds, such as silica and carborundum, are however by far the more important.

Compounds of Silicon

Silica, or Silicon Dioxide, SiO_2, occurs in many different forms in nature. *Quartz*, or rock-crystal, occurs in large transparent six-sided prisms with pyramidal ends. When coloured by manganese and iron compounds, it is called *amethyst*. *Smoky quartz* probably owes its appearance to the presence of organic matter. *Agate*, *Jasper* and *Onyx* are amorphous forms of silica coloured brown or red by ferric oxide, whilst *opal* and *flint* are slightly hydrated forms of silica. *Kieselguhr*, another form of silica, is composed of the shells of marine organisms known as diatoms. Its tubular structure makes it useful as a filter bed for clarifying sugar solutions and oils, and also to absorb liquids, as for example nitroglycerine in the manufacture of dynamite. *Sand* is a partly disintegrated quartz, more or less contaminated with ferric oxide.

Silica exists in three crystalline forms, which are stable in the temperature ranges indicated below—

$$\xrightarrow[\text{quartz}]{} 870^\circ \xleftrightarrow[\text{tridymite}]{} 1470^\circ \xleftrightarrow[\text{cristobalite}]{} 1710^\circ\text{C (m.p.)}$$

Each form also exists in a high temperature and low temperature modification (termed α and β respectively), with a transition temperature of 573°C for the α–β quartz transition.

Properties of Silica. Silica is the only oxide capable of forming an insoluble glass by itself. A transparent form of quartz glass is prepared in relatively small quantities by melting quartz in the oxy-hydrogen flame. Non-transparent silica glass is manufactured in comparatively much larger quantities in tubes up to 4 in. or more in diameter by fusing white sand around an electrically heated central rod at a temperature of 1800° to 2000°C, and then drawing out the still plastic silica tube to form tubes of smaller diameter. The presence of numerous very small air bubbles in the resulting silica accounts for its characteristic lustrous appearance.

The importance of silica-ware and of quartz glass is due mainly to the extremely small coefficient of thermal expansion of silica, and to a smaller extent to its good acid-resisting qualities. The former property accounts, for example, for its ability not to crack when plunged red-hot into cold water. With ordinary glass similarly treated, the strain set up by the rapid contraction of the outer surfaces causes it to break up into small pieces. Silica-ware should not however be subjected to temperatures greater than 1000°C for any considerable length of time, since the polymorphic change to the crystalline tridymite form which occurs slowly at this temperature will introduce weaknesses.

Naturally occurring quartz finds many uses in optical apparatus as lens and prisms, owing to its property of transmitting all light (ultra-violet, visible and infra-red) with minimum of absorption.

Chemically, silica is very stable and relatively inert, as indicated by its high heat of formation—

$$Si + O_2 = SiO_2 + 191\,000 \text{ cal.}$$

It is insoluble in water, and is not attacked by acids, with the exception of hydrofluoric acid—

$$SiO_2 + 4HF = SiF_4 \uparrow + 2H_2O$$

but dissolves in alkalis on boiling to form silicates—

$$2NaOH + SiO_2 = Na_2SiO_3 + H_2O$$

It is thus an acidic oxide like carbon dioxide, and like this oxide its corresponding acid, silicic acid, is extremely weak. It differs however from carbon dioxide in many other respects, particularly those which concern its physical properties.

Silicic Acid. Numerous silicates are known, but the corresponding acids have only a hypothetical existence and consist of more or less indefinite hydrates of silica. When a solution of a soluble silicate, such as

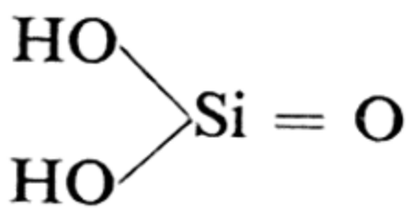
"water glass" (sodium silicate) is acidified with hydrochloric acid, a gelatinous form of silicic acid is obtained—

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$$

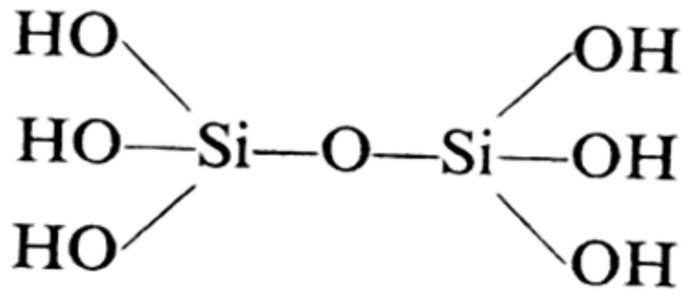
If, however, the silicate solution is poured into excess of hydrochloric acid, the silicic acid remains in colloidal solution. The sodium chloride and excess of hydrochloric acid may then be removed by dialysis (*see* p. 338). When the gelatinous silicic acid is dried, it gradually loses water to form ultimately silica. Orthosilicic acid, H_4SiO_4—($SiO_2 . 2H_2O$)—and metasilicic acid, H_2SiO_3—($SiO_2 . H_2O$)—are thought to occur intermediately during this process. Incompletely dehydrated silicic acid is known as *silica-gel*, and may contain from 5–7 per cent of water. It is used as an absorbent material for recovering valuable vapours (such as carbon disulphide, acetone, and other volatile organic solvents) from the gas effluent in certain industrial processes. The solvent is subsequently recovered by heating the gel, and the latter is then ready for re-use. Silica-gel is also used in many air-drying plants in commercial practice. The spent silica-gel is periodically reactivated by heating (to drive off the moisture) and so may be used over and over again.

The Silicates. The determination of the structure of the many mineral silicates was one of the first major problems in inorganic chemistry to yield to the new methods of X-ray crystal structure analysis. The older ideas regarded the silicates as salts of various complex silicic acids, such as—

(orthosilicic)



(metasilicic)



(orthodisilicic acids)

and so on.

W. L. Bragg was able to show that the silicates are based on a silicon-oxygen framework made up of $(SiO_4)^{4-}$ tetrahedra, in which the four oxygen atoms are arranged at the corners of an imaginary regular tetrahedron with the silicon atom at the centre—

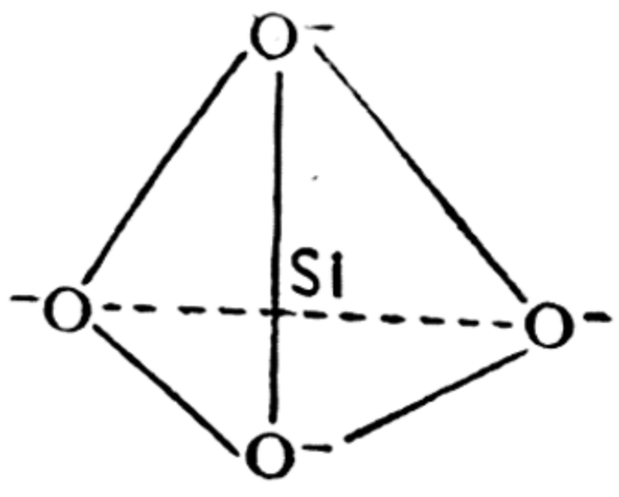


FIG. 192. SiO_4''

These tetrahedra are linked to other such tetrahedra through the oxygen atoms, so that the latter form a part of the two adjacent tetrahedra—

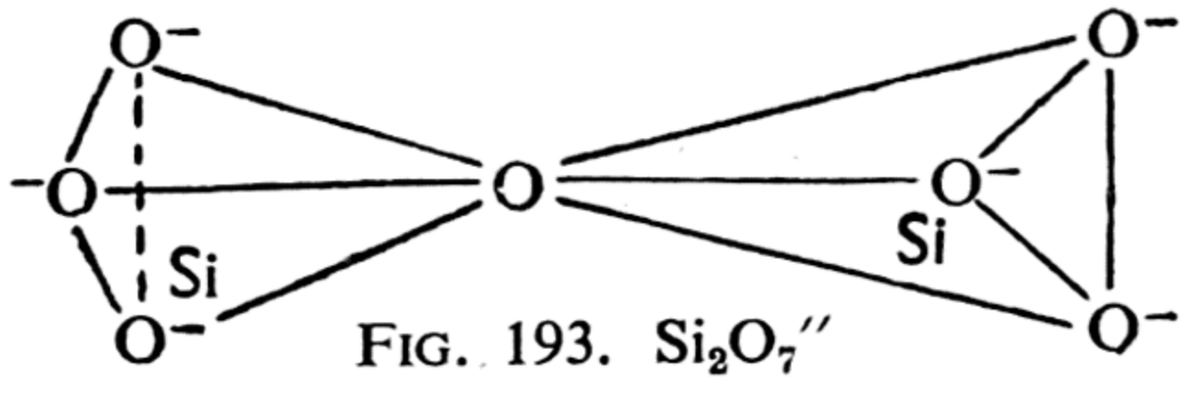


FIG. 193. Si_2O_7''

and this linking up process at the corners of the tetrahedra may be extended to form complex linear, planar or even three dimensional silicon-oxygen skeletons. The negative charges possessed by these complex groupings are balanced by the presence in the interstices of the structure of certain metallic ions, the molecule as a whole then becoming electrically neutral.

Before going on to discuss the various ways in which the silicon-oxygen tetrahedra may link up, it is pertinent to point out the essential difference between the complex compounds of carbon and of silicon. The almost unlimited number of carbon compounds which make up organic chemistry are due primarily to the ability of carbon atoms to link up with other carbon atoms, apparently without limit save that the valency requirements always be satisfied, without becoming unstable. That silicon does not possess this property to any significant extent is evident from the absence of any extensive "organic" chemistry of this element, and by the fact that the relatively few silicon hydrides which have been isolated become increasingly less stable with increase in the Si—Si chain length. When however the silicon atoms are linked together through oxygen atoms, as —Si—O—Si—, this decrease in stability does not occur, and stable molecules based on an indefinitely large framework of silicon and oxygen atoms are formed, as in silica, the silicates and the more recently discovered silicone plastics. The Si—O—Si linkage thus plays a similar part in the chemistry of silicon as the C—C linkage does in the organic chemistry of carbon.

The structures of the silicates may now be discussed in terms of the various ways in which the silicon-oxygen tetrahedra may link up.

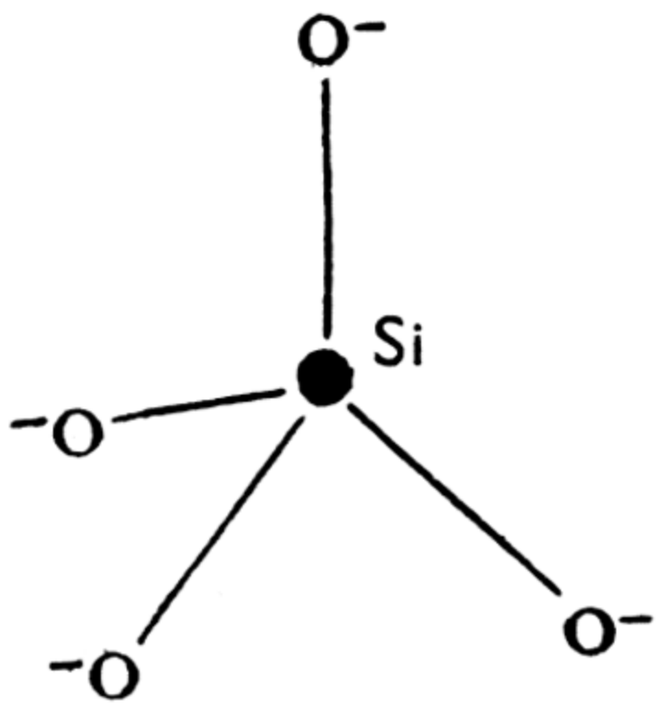
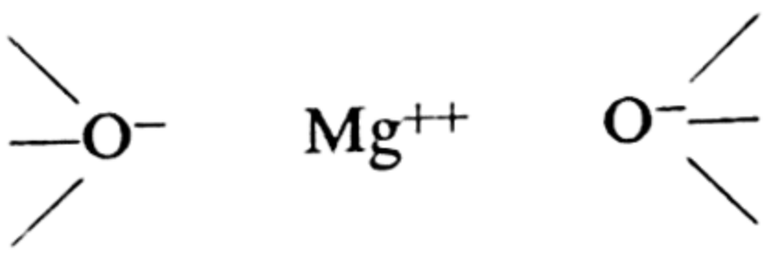


FIG. 194. SiO_4

(*a*) The simplest case is found in the ortho-silicates in which each (SiO_4) tetrahedron occurs as a separate entity. These tetrahedra are linked together ionically through the metal ions, for example—



Examples include *Olivine*, Mg_2SiO_4, *Phenacite*, Be_2SiO_4, and *Zircon*, $ZrSiO_4$.

(*b*) When two $(SiO_4)^{4-}$ tetrahedra are linked together, the group $(Si_2O_7)^{6-}$ is formed having a negative valency of six, the charge being determined by the number of unshared oxygen atoms. An example of this type of structure is found in *Thorveitite*, $Sc_2Si_2O_7$.

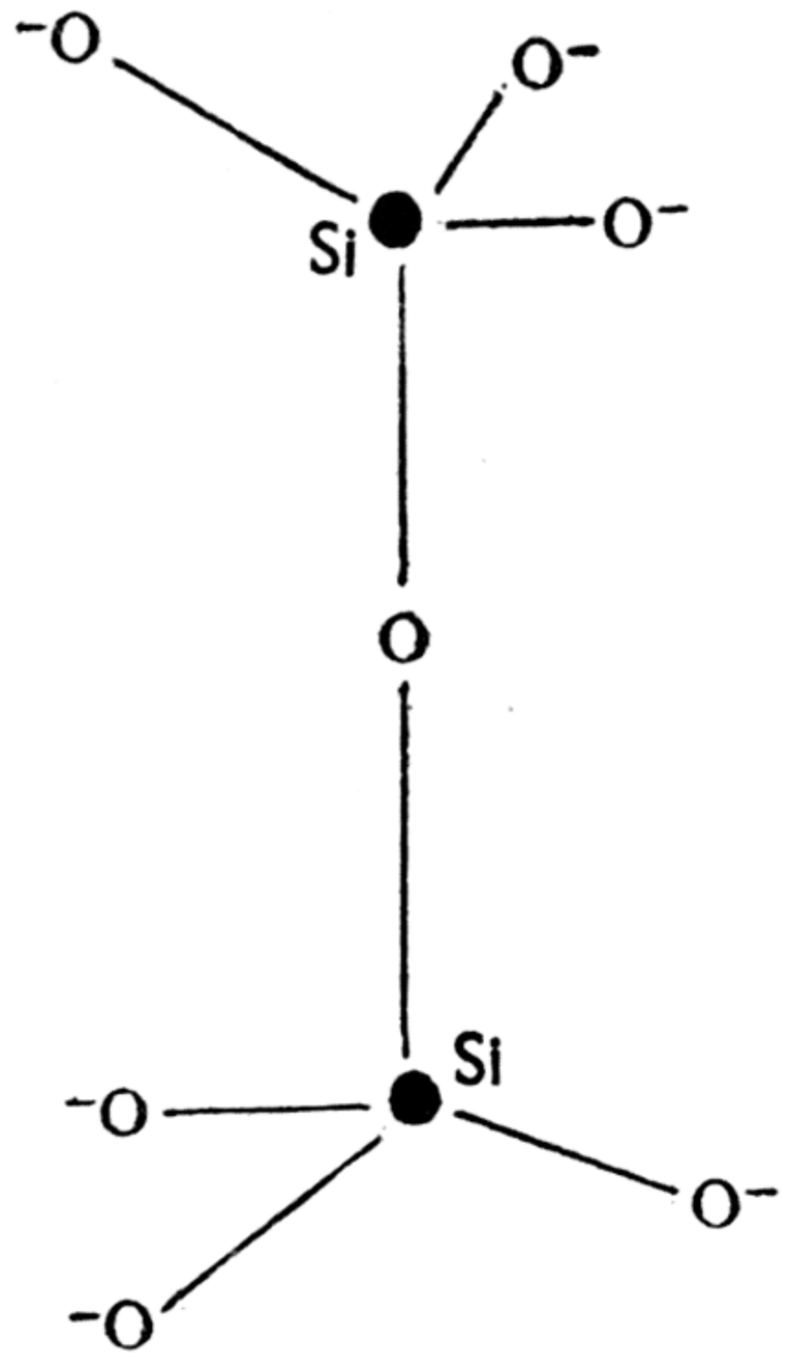


FIG. 195. Si_2O_7

(*c*) *Ring Structures* result when three or more (SiO_4) tetrahedra are linked together in this way, and these may be represented in terms of the planar convention of organic chemistry (*see* p. 852 *et seq.*) as—

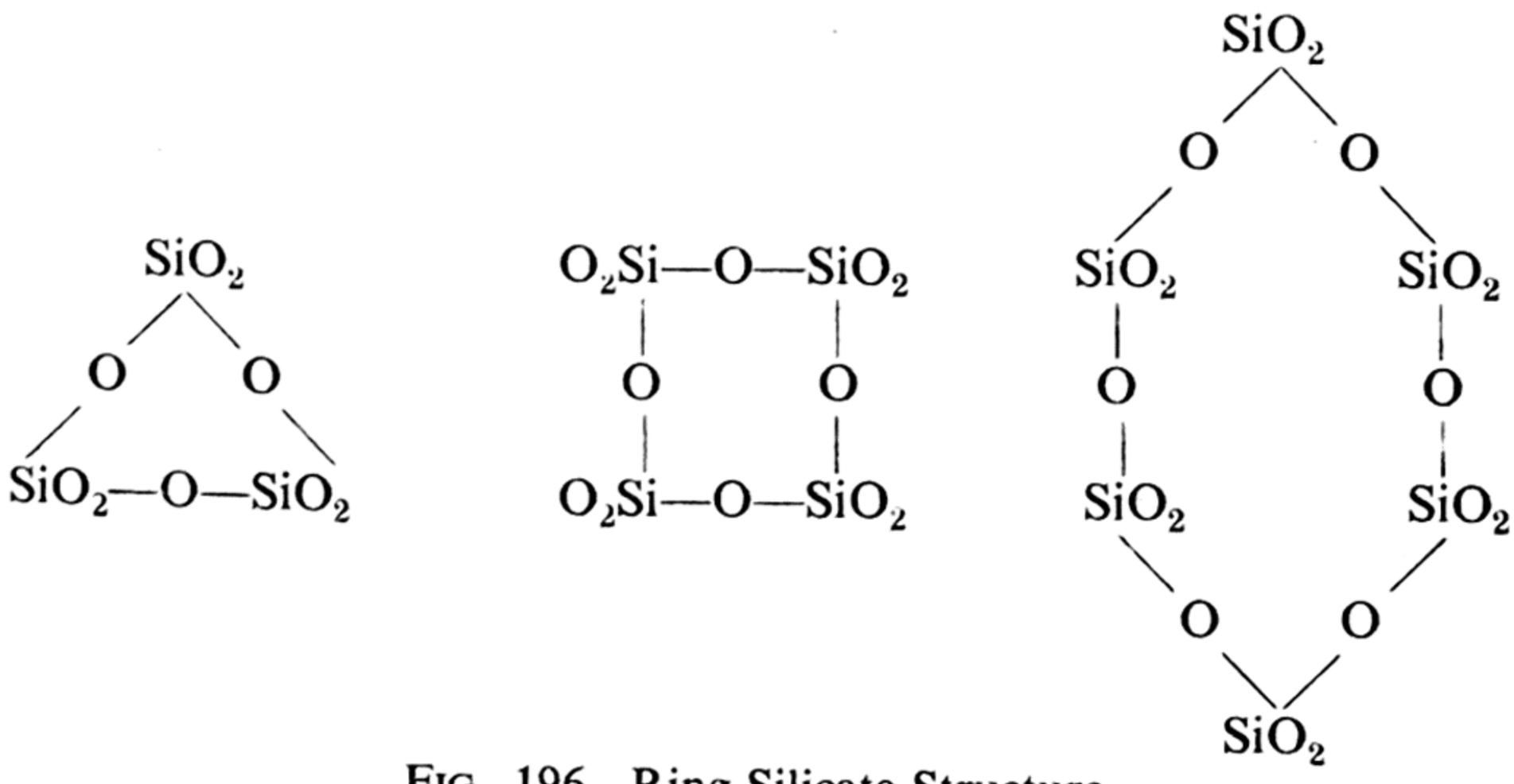


FIG. 196. Ring Silicate Structure

It will be observed that in these ring structures, the silicon:oxygen ratio is 1:3, and that the silicon-oxygen part of the silicate molecule has

the composition $(SiO_3)_n^{2n-}$. Examples of such ring structure silicates include *Benitoite*, $BaTiSi_3O_9$, and *Beryl*, $Be_3Al_2Si_6O_{18}$.

(*d*) When the closed rings of (SiO_4) tetrahedra, each sharing two corners with adjacent tetrahedra, contain an infinite number of such groups, the structure degenerates into extended straight chains of the type: —O—SiO_2—O—SiO_2—O—SiO_2— . . . . This type of structure is found in the *Pyroxene* minerals, of which *Diopside*, $\{CaMg(SiO_3)_2\}_n$ is a typical example.

(*e*) The closely related *Amphibole* minerals have a similar chain-like structure in which two pyroxene type chains are linked together through alternate tetrahedra, the latter thus forming three Si—O—Si linkages, thus—

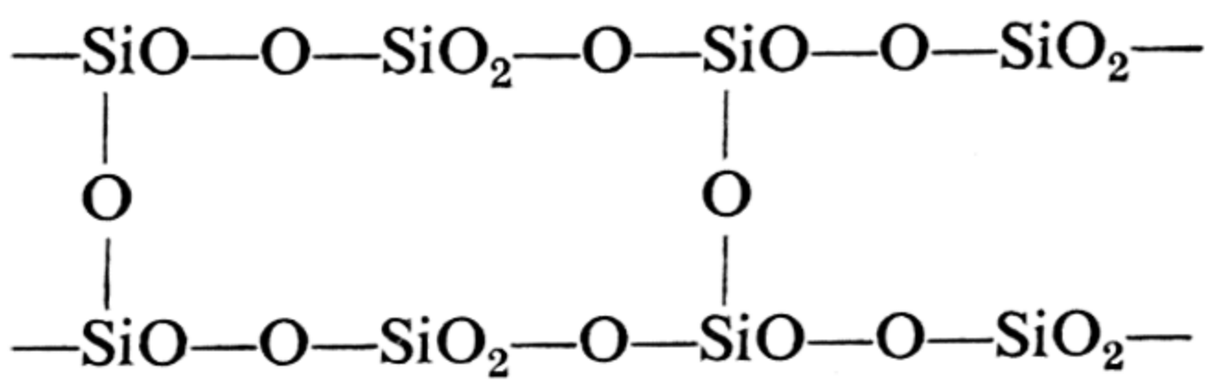


FIG. 197. Amphibole Structure

In these structures, the silicon:oxygen ratio is 4:11. The chain-like structure of both the pyroxene and amphibole minerals accounts for their familiar fibre-like nature, since any cleavage must take place parallel to the length of the chains. *Asbestos* is a typical example of an amphibole mineral.

(*f*) When each (SiO_4) tetrahedron shares three corners with other tetrahedra, the relatively open, sheet-like structure found in the *Micas* is obtained, and the silicon:oxygen ratio is increased to 4:10.

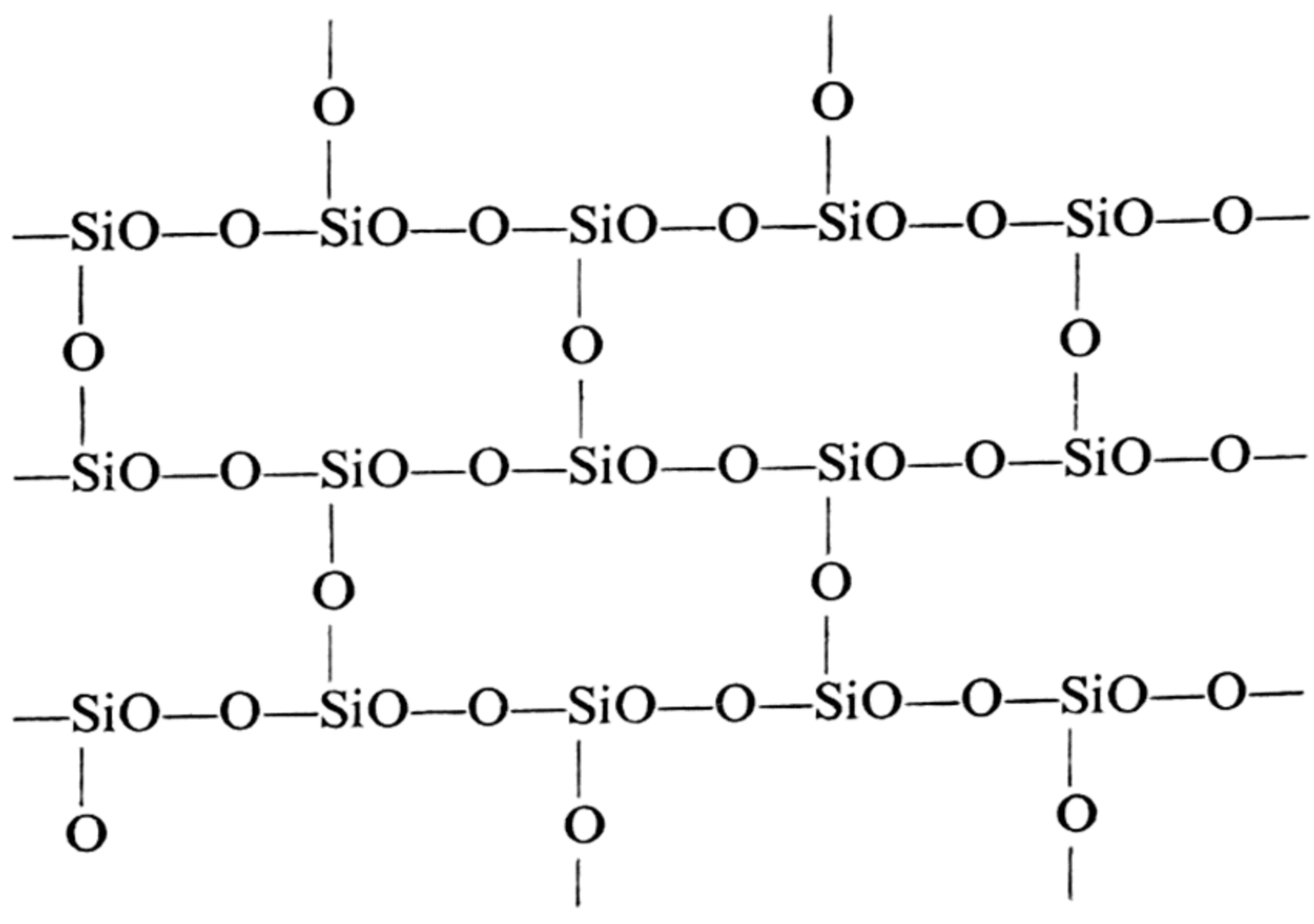


FIG. 198. Mica Structure

In many of these structures, some of the silicon atoms are replaced by aluminium atoms, the net result of which is to increase the negative charge by one for each silicon so replaced. This increase is balanced by the inclusion in the interstices of the structure of an additional metallic ion, as for example, in *Muscovite Mica*, $[(OH)_2KAl_2(Si_3Al)O_{10}]_n$. The planar, sheet-like nature of these silicates accounts for the well-known ease with which mica can be split into thin plates.

(*g*) The final class of silicate structures, the so-called *framework structures*, result when all the corners of the (SiO_4) tetrahedra are linked to other tetrahedra. Such an arrangement results in an indefinitely extended three-dimensional, relatively open framework having an Si : O ratio of 1 : 2. The simplest example of this structure is found in the various forms of silica (quartz, crystobalite and tridymite). When some of the silicon atoms are replaced by aluminium atoms, the resulting increase in negative charge is compensated as before by the inclusion of metallic ions in the interstices of the structure. By far the most important such framework structures occur in the *Felspars*, such as *Orthoclase*, $[K(Si_3Al)O_8]_n$, and also in the *Zeolites*. The structures of the latter accounts for their two very interesting properties—

(i) They contain more or less water which can easily be removed by heating without impairing the rigid silicon-oxygen framework. This water is often referred to as *zeolitic water* in distinction to water of crystallization, the removal of which destroys the crystal structure of the compound. It is explained by the very open nature of the zeolite framework, which is intersected by wide channels through which water molecules (and other solvent molecules) may easily pass without influencing the structure as a whole; and

(ii) The cations can be substituted reversibly by other cations, again without impairing the zeolite structure. This interesting property accounts for the increasing use of zeolites in the base-exchange type of water-softeners (*see* p. 512).

Recapitulating, the silicate structures are based on the various ways in which the SiO_4 tetrahedra may link up, and are not derived from complex silicic acids the existence of which is extremely doubtful. Replacement of silicon by aluminium sometimes occurs, and each such replacement produces a net increase of one negative charge which is balanced by the presence of a suitable metallic ion in the interstices of the structure as shown on p. 606.

Silicon Hydrides or Silanes. Silicon resembles carbon in forming a number of hydrides, which differ however from those of carbon in that they all belong to the saturated series (*see* p. 859), for example

$$SiH_4,\ Si_2H_6,\ Si_3H_8,\ Si_4H_{10},\ \text{etc.},$$

and also in the relative instability of the higher members and in their much higher reactivity. The latter is to be anticipated from the pronounced tendency of silicon to combine with oxygen rather than with itself, so that the hydrides might be expected for example to react more or less readily with oxygen-containing compounds.

TABLE 94

Silicate Structure Types

Structure	Example	Si:O Ratio
Isolated tetrahedra	Orthosilicates, e.g. olivine	1:4
Two tetrahedra, sharing one corner . .	Thorveitite	2:7
Closed rings of tetrahedra, each sharing two corners	Benitoite, Beryl	1:3
Infinite chains, each tetrahedra sharing two corners	Pyroxene	1:3
Infinite double chains of tetrahedra, sharing alternately two and three corners	Amphiboles	4:11
Infinite sheets of tetrahedra each sharing three corners	Micas	2:5
Infinite three-dimensional framework structures, each tetrahedra sharing all four corners	Felspars, Zeolites, Quartz	1:2

The silicon hydrides were first prepared by Stock by a method which recalls his preparation of the boron hydrides. Magnesium silicide, prepared by heating magnesium and silicon together in the absence of air, was treated with 20 per cent hydrochloric acid, and the resulting hydrides condensed in a trap immersed in liquid nitrogen. Fractional distillation of the condensate in a vacuum apparatus enabled small quantities of the hydrides, listed above, to be separated—

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$$

Monosilane, SiH_4, is however more easily prepared by using a solution of ammonium bromide in liquid ammonia in place of the acid to decompose the magnesium silicide, and carrying out the reaction at $-30^{\circ}C$ in a slow stream of hydrogen.

Compared with the corresponding carbon compounds, the silanes are less volatile (that is, they have higher boiling points), have lower ignition temperatures, and become increasingly more inflammable with increase in

molecular weight. Their stability also rapidly decreases with increase in molecular weight, and they are much more reactive chemically. Thus, they are decomposed by dilute alkalis—

$$SiH_4 + 2NaOH + H_2O = Na_2SiO_3 + 4H_2 \uparrow$$

are strong reducing agents, and will consequently decolorize potassium permanganate solution, reduce mercuric salts to mercurous, ferric to ferrous, and cupric salts to copper hydride. The silanes also react explosively with chlorine and with bromine at ordinary temperatures.

Halogen Compounds of Silicon

Silicon Tetrafluoride, SiF_4. It has already been stated that silicon (and silica) will ignite spontaneously in fluorine to form silicon tetrafluoride. The latter is more easily prepared however by heating a mixture of calcium fluoride and silica with concentrated sulphuric acid—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$
$$SiO_2 + 4HF = SiF_4 \uparrow + 2H_2O$$

This reaction will also occur with any silicate, and is used in gravimetric analysis to determine the proportion of silicon present (as silica). The sample to be analysed is weighed in a platinum crucible of known weight, and repeatedly ignited with small quantities of hydrofluoric acid until no further loss in weight occurs. The loss in weight then gives directly the weight of silicon, calculated as SiO_2, contained in the original sample.

Silicon tetrafluoride is a colourless fuming gas, and is decomposed by water to form silicic acid and hydrofluosilicic acid; the presence of concentrated sulphuric acid in the above method of preparation prevents this hydrolysis by removing the water as it forms—

$$SiF_4 + 3H_2O = H_2SiO_3 + 4HF$$
$$SiF_4 + 2HF = H_2SiF_6$$

hydrofluosilicic acid

The presence of a fluoride in an unknown mixture is sometimes detected by this hydrolysis. The mixture is heated with a little concentrated sulphuric acid, and a moistened glass rod held in the upper half of the test-tube. The liberated hydrogen fluoride attacks the glass to form silicon tetrafluoride which is hydrolyzed by the water on the glass rod to form a white coating of silicic acid.

Hydrofluosilicic acid is a weak acid, and its salts, the fluosilicates are fairly soluble in water, with the exception of the potassium and barium salts which are sparingly soluble. Fluosilicates and hydrofluosilicic acid are used, like the fluoborates, in certain plating solutions and in the electrolytic recovery of some metals, for example in the production of lead of

99·99 per cent purity. The electrolyte is an aqueous solution of lead fluosilicate (containing about six per cent lead), to which is added about 10 per cent of hydrofluosilicic acid. Gold, silver and bismuth remain undissolved at the anode, forming a slime which is collected and subsequently worked up for these metals.

Silicon Tetrachloride, $SiCl_4$, is usually prepared by passing dry chlorine over a heated mixture of silica and carbon—

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$$

but it may also be prepared by the direct action of chlorine on silicon, silicon carbide or ferrosilicon, when these latter are heated.

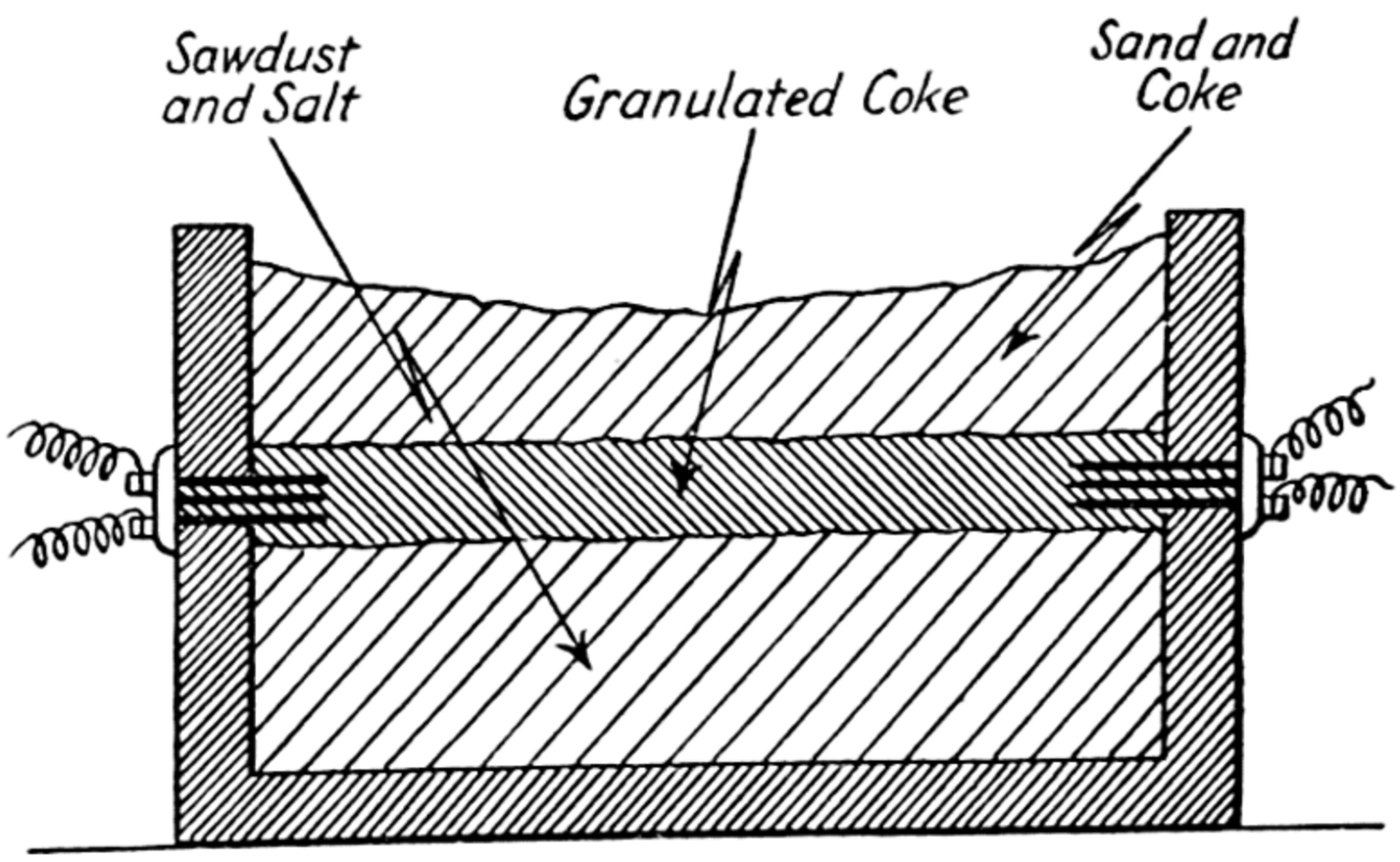


FIG. 199. Electric Furnace for the Manufacture of Calcium Carbide

Silicon tetrachloride is a colourless fuming liquid which may be purified from excess of chlorine by shaking with mercury and then redistilling. It boils at 58°C and freezes at − 89°C, and when hydrolyzed by water forms silicic acid and hydrochloric acid—

$$SiCl_4 + 3H_2O = H_2SiO_3 + 4HCl$$

Silicon Carbide (Carborundum), SiC, is manufactured by heating a mixture of sand and coke together in an electric furnace, such as the Acheson furnace used at Niagara.

The furnace charge consists of equal parts of sand and coke mixed with a little salt and sawdust. This mixture is packed around a core of granulated coke which separates the two electrodes. The salt acts partly as a flux and partly to form chlorides with any metallic impurities present, whilst the sawdust helps to make the charge porous. After about 36 hours, during which carbon monoxide gas is evolved, the current is cut off and the furnace allowed to cool. The furnace is then dismantled, and the carborundum is found separated by a layer of graphite from the core between the two electrodes.

Carborundum is nearly as hard as the diamond, a property which accounts for its use in carborundum wheels as an abrasive. It is remarkably resistant to most chemicals including acids, but is attacked by fused alkalis. This resistance to chemical attack explains its use in the manufacture of refractory materials, for example for furnace linings.

Glass

Glass is essentially a mixture of various metallic silicates which have not crystallized out on cooling from the fused state. Only the silicates of sodium and potassium are soluble in water, but if these are fused with other silicates, such as calcium silicate, the resulting glass becomes insoluble in water. The presence of the alkali silicate considerably lowers the fusion temperature (and so facilitates the glass manufacture) of the mixture, but the proportion must not be excessive since the resulting glass becomes appreciably soluble. The simpler lime-soda glasses probably consist of a solution of silica in a mixture of sodium and calcium silicates, in which the three major constituents are regarded analytically as a mixture of (*a*) the basic oxides, sodium and calcium oxides, and (*b*) the acidic oxide, silica. It is only a small step to the more general statement that glass is essentially a mixture of solid solutions (which has not crystallized on cooling from the fused state) of acidic oxides, such as silica, boric oxide, phosphoric oxide, etc., and metallic (basic) oxides, such as those of the alkali and alkaline earth metals and lead. Variations in the nature and proportion of these constituents, together if desired with the addition of colouring materials, then accounts for the very considerable number of substances which possess the characteristic properties of glass. They are amorphous, hard, brittle substances, which break with a conchoidal fracture and are usually transparent but may be translucent or even opaque.

Their method of manufacture may be illustrated by reference to the procedure for making lime-soda glass. A charge, consisting of a mixture of sodium carbonate and sodium sulphate with calcium carbonate (or lime) and silica (sand), is mixed with ground scrap glass (*cullet*) and melted in a large tank lined with fire-brick, or in covered fire-clay crucibles. The cullet is added to facilitate the fusing operation. The reaction occurs slowly and the temperature has to be controlled between certain limits. The liberation of carbon dioxide—

$$SiO_2 + CaCO_3 = CaSiO_3 + CO_2 \uparrow$$

causes the fused mass to boil, and when this ceases the "metal," (i.e. glass) is ready for fabricating into the finished article. Since glass, as normally cooled, is in a state of strain (due to its uneven contraction) it is necessary to anneal the glass. In this operation, the glass is raised to a temperature just below its softening-point, and then allowed to cool very slowly; the thicker the glass the longer the time required for cooling.

Coloured glass is produced when certain metallic oxides (see "borax bead tests") or other substances are included in the charge. These include the various oxides of iron, copper, chromium, manganese, cobalt, nickel and the rare earths, and also neutral materials such as carbon (blackening), sulphur (amber), silver (yellow) and selenium, copper, or gold (ruby red). Traces of manganese dioxide are often added when making common glass in order to decolorize the yellow or green colours imparted to the glass by the iron oxide impurities present in the sand.

Bohemian or Hard Glass has a much higher softening temperature than lime-soda glass and is prepared by substituting potassium carbonate for the sodium compounds.

Lead Glass or Flint Glass, used for example in making "cut-glass" articles, has a high refractive index. It is made by replacing most of the sodium compounds with lead dioxide, the latter forming lead silicate.

Pyrex Glass, and other boro-silicate glasses (Monax, Hysil) owe their important properties of resistance to temperature change and to mechanical shock, to the presence of up to 12 per cent of boric oxide. Boric oxide in glass has a negative coefficient of thermal expansion up to 12 per cent concentration, but above this concentration, the sign of the coefficient changes. Pyrex glass contains about 80 per cent of silica, 12 per cent of boric oxide and only 3–4 per cent of sodium oxide. Its coefficient of expansion is approximately, 0·0000035 per degree Centigrade. An interesting example of its use is in the manufacture of the reflector for the 200-in. telescope in the observatory at Pasadena.

Safety Glass. Laminated safety-glass is manufactured by sandwiching a layer of a tough transparent adhesive material, such as cellulose butyral between two layers of glass. "Toughened Glass" is prepared by rapidly and uniformly cooling the outer surface of glass which has been softened just previously. The sheet of glass to be toughened is supported vertically and heated to its softening point. It is then subjected to a blast of cold air to produce a uniformly strained state in the surface of the glass. Such glass is from six to ten times as strong mechanically as the similar but untreated glass, and when fractured the splinters do not have sharp edges.

Quartz Glass. For an account of quartz glass and silica ware *see* p. 535.

Water Glass. Sodium silicate is manufactured by fusing together a mixture of clean sand and sodium carbonate—

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2 \uparrow$$

The solid product obtained on cooling is broken up and then heated with water and steam under pressure in suitable boilers, when the sodium silicate passes into solution. The resulting solution is then concentrated in evaporators of a special type to produce a very viscous water-white liquid, known as *water-glass*. Water-glass finds many interesting uses, such as in the manufacture of certain brands of fire-clay cements, in the

preserving of eggs (the pores of which are closed by the formation of insoluble calcium silicate), in fire-proofing wood, and as an ingredient in the cheaper varieties of soap.

Clay

Clays are formed by the weathering (i.e. decomposition) of felspathic rocks, and are composed essentially of hydrated aluminium silicates, such as, $Al_2Si_2O_7 \,.\, 2H_2O$, together with other substances, such as mica and quartz which were present with the felspar in the original rocks (e.g. granite)—

$$2KAlSi_3O_8 + 2H_2O + CO_2 = Al_2Si_2O_7 \,.\, 2H_2O + 4SiO_2 + K_2CO_3$$

The purest clay in this country is found in Cornwall (St. Austell) and in Dorsetshire (Wareham), and is known as "china clay." It is produced as described above by the weathering (or *kaolinization*) of felspar, which softens the latter so that it may easily be broken up. In practice this breaking up is effected by directing powerful jets of water on to the face of the rock, the water carrying away the decomposed felspar together with the quartz and mica present in the original granite rock. The coarse sand settles out in sand pits, and the water (with its suspension of clay) is then made to flow slowly over a series of terraces to enable the mica to settle out, before passing into the clay pits. Here, the water is partially separated and the clay then transferred to storage tanks where it is further dehydrated to the consistency of butter. Final drying is then effected by the combined action of filter presses and artificial heating.

China clay is second only to coal, on a tonnage basis, as an export material. Apart from its use in the manufacture of ceramics (pottery, porcelain, china-ware), considerable quantities are used in paper-making to "load" the paper (particularly in newsprint because of its cheapness and because it helps to absorb the ink), and as a cheap white filler in the soap, paint and rubber industries.

Ceramics. The term "ceramic" is applied in general to anything made by heating clay (pottery, porcelain, stone-ware, bricks, etc.). Ordinary clay is a plastic, thixotropic material, which hardens irreversibly when heated sufficiently strongly. The occluded water and water of hydration is first lost at about 400°–700°C, and above this temperature the alumina and silica react to form a new anhydrous aluminium silicate, the reaction being complete at 1100°–1200°C. The resulting burnt clay will not recombine with water, and so does not soften and reform the initial hydrated plastic clay—

$$Al_2Si_2O_7 \,.\, 2H_2O \xrightarrow{400°–700°C} Al_2Si_2O_7 \xrightarrow{700°–1200°C} \textit{Ceramic}$$

The two important properties of clay are thus seen to be—

(*a*) Its plastic nature, which enables it to be moulded into articles of different shape and size, and

(*b*) its behaviour when heated strongly, or *fired*, to form a permanently hard, practically infusible solid.

Bricks, tiles, and ordinary red and brown stone-ware are produced by firing clay, more or less contaminated with oxides and various other impurities. Small quantities of old brick are usually incorporated in the finely-divided state (*grog*) to prevent undue shrinkage during the firing operation. The porous products are often rendered impermeable by surface glazing. The purer forms of clay, for example china clay, are used in the manufacture of porcelain and china-ware. These are non-porous, but may be glazed for decorative purposes and also to produce surfaces which keep clean. A simple method of glazing applicable to ordinary earthenware is to throw common salt into the kiln. The salt reacts with the steam to form sodium hydroxide—

$$NaCl + H_2O = NaOH + HCl$$

which then attacks the silica to form sodium silicate. This then reacts further to form a complex insoluble fusible silicate, resembling glass. More usually, the article is coated with a glazing material, consisting of felspars (or other alkali alumino-silicate), boric oxide or lead oxide, and given a short heat treatment to form a surface glassy layer of a boro-silicate or lead silicate.

Refractories. A refractory material is one which not only has a relatively high fusion point, but in the industrial sense of the term, must also be able to withstand the corrosive action of molten slags and glasses, have relatively high mechanical strength, and possess a low heat conductivity. They are classified into three main types, based on the chemical properties of the constituent substances—

(*a*) *Acid Refractories.* The most important acid refractories are made from silica and silicates (fire-clay). Relative freedom from impurities such as oxides of iron (which react for example with reducing gases in the blast-furnace), calcium and magnesium carbonates, and alkali compounds, is desirable since the presence of such impurities, as a result of lowering the melting point, may lead to ultimate break-down of the refractory bricks. The latter are prepared, after drying the moulded clay bricks, by firing for about three days at a temperature of approximately 1400 C. Silica bricks are manufactured similarly, using materials with a very high silica content, such as Dinas rock (95 per cent SiO_2), sandstone, white-sand, etc.

(*b*) *Basic Refractories.* The most important basic refractories are prepared from magnesite and dolomite. These are calcined at a white heat to produce the oxides and liberate carbon dioxide. After powdering, these are then moulded into bricks and fired at a high temperature. Such basic refractories are used for example in the basic open-hearth steel furnaces.

(*c*) *Neutral Refractories.* The most important neutral refractories are made from carbon (graphite or plumbago) and from chromite. The latter is a naturally occurring ore, $FeOCr_2O_3$, with a very high melting point. After powdering it is mixed with a little clay (which serves as a binder), moulded into bricks, and fired in the usual way.

Other refractories, not usually classified in one or other of the above groups, include those made from sillimanite (aluminium silicate), bauxite (aluminium oxide), zirconia (zirconium oxide) and silicon carbide. Silicon carbide bricks have a very high fusion point (greater than 2000°C) and have a heat conductivity about ten times that of ordinary fire-brick, properties which account for its increasing use in certain parts of furnaces.

TIN

Occurrence. Metallic tin does not occur in the free state in nature, and practically the whole of the world's supply of the metal is obtained from one mineral only, namely, *cassiterite*, SnO_2. This mineral is often contaminated with other minerals such as arsenical pyrites, copper pyrites, tungstates, etc. Cassiterite is obtained both from lodes as well as from alluvial deposits. The tin content in some of these deposits of cassiterite is less than 1 per cent. The world's chief tinfields are located in Malaya, Burma, Siam, the Netherlands East Indies, Bolivia, Nigeria, the Belgian Congo, and China. By far the greatest production in all these, except Bolivia, is from alluvial and detrital deposits, such deposits yielding about three-quarters of the world's tin. Tin ore is one of the few important industrial ores not found in the U.S.A. The deposits in Bolivia are mostly vein formations. Some tin as cassiterite occurs in vein deposits in Cornwall.

Extraction of Tin

Mining and Concentration. Much of the cassiterite is mined by hydraulic methods in which the ore is sluiced out of the surrounding ground, the sand and gravel being treated in sluice boxes to concentrate the cassiterite and wash out the worthless gangue material. Also of importance are dredging methods in which the tin-bearing mud (sometimes containing only one part of cassiterite in 8000 or even 10 000 parts of alluvial silt) is lifted from the bottom of a lake. A modern tin dredge is much more than an excavating mechanism, however, since by a complex system of screens and jigs the tin-bearing mud is sorted out mechanically on board the dredge, until a concentrate carrying 35 per cent of tin ore is obtained.

Tin ore from vein deposits is first crushed and then subjected to classifying operations to produce a concentrate.

Roasting. The concentrate obtained as described above is roasted in furnaces of the rotating cylinder type. During roasting much of the sulphur and arsenic and some of the antimony are volatilized and removed as their oxides.

If the tin concentrates contain tungsten compounds the material is then heated with sodium carbonate or sodium sulphate at a temperature of about 600°C. The sodium tungstate which is formed is then leached out with water.

Smelting. The roasted (and leached) concentrate is then smelted with carbon in a reverberatory furnace. A temperature of 1200°–1300°C, is employed to ensure adequate liquation of the tin from the slag. The reaction involved is—

$$SnO_2 + 2C = Sn + 2CO \uparrow$$

The metallic tin is tapped off from the bottom of the reverberatory furnace and cast into pigs weighing about 75 lb each.

Refining. The tin obtained from the smelter is refined by liquating in a small sloping-hearth reverberatory furnace, the hearth sloping towards a large door or taphole, which discharges the tin continuously into a large cast iron kettle. This operation of liquation is repeated if necessary. In this refining process most of the iron, copper, arsenic and antimony remain in the furnace as dross; most of the lead and bismuth are retained in the tin.

The tin contained in the cast iron kettle is then heated to a temperature considerably in excess of its melting point and submitted to "boiling," that is a poling operation similar to that employed for the fire-refining of copper (*see* p. 456). The tin produced in this manner has a purity of 99·9 per cent tin.

Physical Properties of Tin

(*a*) Tin is a white lustrous metal, with a slight yellowish tinge.

(*b*) Tin exists in two allotropic forms, the normal, white tetragonal form being stable above 13·2°C, whilst the grey cubic modification is stable below this temperature. The grey form is not readily produced unless the temperature is maintained at a considerably lower value than 13·2°C. Small contents of bismuth, antimony and lead, such as are often present as impurities, exhibit a strong inhibitive effect on the transformation. At 170°C tetragonal tin passes into rhombic tin.

(*c*) Tin has a low melting point (232°C), but a high boiling point (2270°C).

(*d*) Tin is a soft metal which flows readily under pressure and may readily be rolled into foil or extruded into tubes, although it is not easily drawn into fine wire. During the deformation of metallic tin (and certain tin-rich alloys) the so-called "cry" of tin is heard; this is due to the movement of crystal blocks by the deformation process.

Chemical Properties of Tin

(*a*) Tin is not affected by air at atmospheric temperature, but when

heated in air to a temperature of 1500°–1600°C, the metal takes fire burning with a white flame to form stannic oxide, SnO_2.

(*b*) Tin is not affected by water, hence this characteristic in conjunction with that last named makes tin a suitable metal for protecting other more easily corrodible metals, for example iron and steel.

(*c*) It does not combine directly with nitrogen and carbon, and only forms slight traces of stannic hydride, SnH_4, when stannic oxide is reduced with hydrogen.

(*d*) Tin combines directly with chlorine to give stannic chloride, $SnCl_4$; and with sulphur when heated to form stannous sulphide, SnS.

(*e*) Dilute hydrochloric acid only attacks tin slowly forming stannous chloride and liberating hydrogen, but the concentrated acid attacks the metal rapidly.

Dilute sulphuric acid reacts to form stannous sulphate and liberate hydrogen whilst the concentrated acid leads to the evolution of sulphur dioxide instead, thus—

$$Sn + 2H_2SO_4 = SnSO_4 + SO_2\uparrow + 2H_2O$$

The action of nitric acid varies according to the temperature, and the concentration of the acid. Thus cold dilute nitric acid forms stannous nitrate and ammonium nitrate—

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

On the other hand nitric acid of about 50 per cent strength yields copious fumes of oxides of nitrogen and a bulky white precipitate of metastannic acid, $H_2Sn_5O_{11} \cdot 4H_2O$.

(*f*) Hot aqueous solutions of caustic alkalis react with tin to form stannates, thus—

$$Sn + 2NaOH + H_2O = \underset{\text{sodium stannate}}{Na_2SnO_3} + 2H_2\uparrow$$

Uses of Tin. Owing to its good resistance to corrosion under a wide variety of conditions the major use of tin is in the form of coatings for steel and for copper. Nearly 40 per cent of the world's tin consumption is accounted for by tinplate which is used for cans for food packing, and for a large variety of sheet metal articles. Tin coatings, applied by hot-dipping, electrodeposition and by metal spraying, are also widely used for articles employed in the handling of water, milk and food products.

Copper wire which is to be insulated with vulcanized rubber is first tinned, in order to protect it from attack by sulphur.

Electrodeposited tin coatings are often applied to cast iron and aluminium alloy pistons used in internal combustion engines, in order to facilitate "running-in."

The metal is also used in the form of piping for alcoholic liquors, and

distilled water, as collapsible tubes for toilet preparations, and as foil for wrapping cheeses and other products.

Tin is an important constituent of many important industrial alloys; some of the more common are as follows.

TABLE 95

Typical Compositions of some Common Tin Alloys

Name of Alloy	Percentage Composition by Weight							
	Sn	Pb	Cu	P	Zn	Sb	Bi	Cd
Soft solders—								
(*a*) Tinman's solder . .	62·0	38						
(*b*) Plumber's solder . .	33·0	67						
Coinage bronze . . .	4·5		95·5					
Cast phosphor bronze . .	12·0		87·5	0·5				
Gunmetal	10·0		88·0		2			
Bell metal	25·0		75·0					
Type metal . . .	20·0	54	1·0			25		
Wood's metal . . .	12·5	25					50	12·5

Compounds of Tin

Tin forms two series of compounds, stannous compounds in which a valency of two is exhibited, and stannic compounds in which tin has a valency of four.

The stannous compounds are largely salt-like in character.

Stannous Oxide, SnO. This compound is prepared either by heating stannous oxalate,

$$SnC_2O_4 = SnO + CO\uparrow + CO_2\uparrow$$

or by carefully heating stannous hydroxide in a stream of carbon dioxide,

$$Sn(OH)_2 = SnO + H_2O$$

Stannous oxide is very easily oxidized, exposure to the air converting it to the stannic oxide.

Stannous Hydroxide $Sn(OH)_2$ is prepared by the addition of an alkali to the solution of a stannous salt, thus—

$$SnCl_2 + 2NaOH = Sn(OH)_2\downarrow + 2NaCl$$

Stannous oxide is a brown (sometimes dark grey) powder which is amphoteric in character; it reacts with acids to give stannous salts, and with caustic alkalis to give stannites.

Stannous Chloride, $SnCl_2$, is prepared by the action of hydrochloric acid upon metallic tin. From this solution the dihydrate, $SnCl_2 . 2H_2O$, often known as "tin salt," crystallizes out. The anhydrous salt is obtained when the dihydrate is heated in a stream of hydrogen chloride. Alternatively, the anhydrous salt may be obtained by heating tin with mercuric chloride, when mercury volatilizes and stannous chloride remains as the residue—

$$Sn + HgCl_2 = SnCl_2 + Hg \uparrow$$

Stannous chloride dissolves readily in water, hydrolysis occurring, and a basic chloride being formed—

$$SnCl_2 + H_2O \rightleftharpoons Sn(OH)Cl \downarrow + HCl$$

Stannous chloride is a powerful reducing agent, for example in aqueous solution mercuric chloride is reduced first to mercurous chloride and finally to mercury, as follows—

(i) $$2HgCl_2 + SnCl_2 = Hg_2Cl_2 \downarrow + SnCl_4$$

(ii) $$Hg_2Cl_2 + SnCl_2 = 2Hg \downarrow + SnCl_4$$

Similarly, ferric and cupric salts are reduced to the ferrous and cuprous states respectively, nitric acid is reduced to hydroxylammine, and chromates to chromium salts. Zinc, however is a more powerful reducing agent and reduces stannous chloride to metallic tin.

Stannous Sulphide, SnS, is formed as a black powder by heating tin and sulphur together. When hydrogen sulphide is passed through the aqueous solution of a stannous salt, *stannous hydrosulphide*, $Sn(HS)_2$ is formed as a brown precipitate; on drying, this precipitate becomes black. Stannous sulphide reacts with yellow ammonium sulphide which converts it to stannic sulphide and thence into the soluble *ammonium thiostannate*, $(NH_4)_2SnS_3$.

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3$$

The stannic compounds are largely covalent in character, though in water the hydrated stannic ion can exist.

Stannic Oxide, SnO_2. This compound occurs in nature as cassiterite, but it may be prepared in the laboratory, either by burning the metal in air, or alternatively by acting upon tin with concentrated nitric acid and calcining the residue obtained.

Stannic oxide is not attacked by acids, except sulphuric acid with which it reacts to form stannic sulphate—

$$SnO_2 + 2H_2SO_4 = Sn(SO_4)_2 + 2H_2O$$

This stannic sulphate is unstable and on dilution with water, stannic oxide is reprecipitated.

Stannic oxide reacts with caustic alkalis to form soluble stannates, thus—

$$SnO_2 + 2NaOH = \underset{\text{sodium stannate}}{Na_2SnO_3} + H_2O$$

In industry, stannic oxide is employed in the manufacture of white glazes, tiles and glass-ware.

Stannic Hydroxide, $Sn(OH)_4$, is prepared by the action of aqueous solutions of caustic alkalis or the carbonates of the alkali metals upon solutions of stannic salts, thus—

$$SnCl_4 + 4NaOH = Sn(OH)_4 \downarrow + 4NaCl$$

The hydroxide is also precipitated when stannic chloride suffers hydrolysis.

$$SnCl + 4H_2O = Sn(OH)_4 \downarrow + 4HCl$$

If stannic oxide is dried in air it yields *orthostannic acid*, $Sn(OH)_4$ or H_4SnO_4, but if dehydrated over concentrated sulphuric acid, *metastannic acid* is formed, $SnO(OH)_2$ or H_2SnO_3. The following outline shows the relationship of these compounds.

Stannic hydroxide, $Sn(OH)_4$

↓

(dried in air)

↓

$Sn(OH)_4$ or H_4SnO_4 — orthostannic acid

↓

(dehydration with concentrated sulphuric acid)

↓

$SnO.(OH)_2$ or H_2SnO_3 — metastannic acid

↓

(this acid exists in two forms, thus)

α-Metastannic acid	β-Metastannic acid
derived from stannic salt solutions by precipitation with alkalis. Salts of this acid yield the $(SnO_3)''$ ion.	derived from the reaction of concentrated nitric acid on tin. This β-metastannic acid is possibly a polymerized form of α-metastannic acid $(H_2SnO_3)_5$

Stannic Chloride, $SnCl_4$ is a colourless fuming liquid made by the action of chlorine on molten tin. When this reaction occurs the stannic chloride volatilizes and is collected in a receiver.

It fumes strongly in moist air, being converted into the pentahydrate $SnCl_4 . 5H_2O$, which is often known as *oxymuriate of tin* or "butter of tin." In the presence of excess water conversion into stannic acid occurs, thus—

(i) $$SnCl_4 + H_2O \rightleftharpoons Sn(OH)Cl_3 \downarrow + HCl$$

(ii) $$Sn(OH)Cl_3 + 3H_2O \rightleftharpoons Sn(OH)_4 \downarrow + 3HCl$$

Stannic chloride forms a series of complex salts, of which the most important is *ammonium chlorostannate*, or "Pink salt," $(NH_4)_2SnCl_6$.

Both stannic chloride and pink salt are used as mordants in the dyeing industry.

Stannic Sulphide, SnS_2, is precipitated when hydrogen sulphide is passed through an aqueous solution of a stannic salt which has previously been acidified.

Crystalline stannic sulphide, often known as "mosaic gold" is made by heating a mixture of powdered tin, sulphur and ammonium chloride.

(i) $$Sn + 4NH_4Cl = (NH_4)_2SnCl_4 + H_2 + 2NH_3$$

(ii) $$2[(NH_4)_2SnCl_4] + 2S = SnS_2 + (NH_4)_2SnCl_6 + 2NH_4Cl$$

Stannic sulphide dissolves in colourless ammonium sulphide to yield ammonium thiostannate—

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

and in aqueous solutions of alkali metal hydroxides to form a mixture of the thiostannate and stannate of the alkali metal, thus—

$$3SnS_2 + 6NaOH = 2Na_2SnS_3 + Na_2SnO_3 + 3H_2O$$

LEAD

Occurrence. Lead sulphide occurring in nature as *galena*, PbS, is by far the most important source of the world's lead. This mineral invariably contains some silver, often in sufficiently high content to permit of its profitable extraction. Other lead ores of importance are *cerrusite*, $PbCO_3$ and *anglesite*, $PbSO_4$. Zinc is often found as sulphide along with lead ores. The world's largest producers of lead ore are Australia (Broken Hill), Colorado and the Tri-State field of the U.S.A. (Missouri, Oklahoma and Kansas), British Columbia, Burma, Mexico, and the U.S.S.R.

Extraction of Lead

The chief processes involved in the extraction of lead are as follows.

Concentration. Before being sent to the smelter it is necessary to remove as much of the impurities as possible. As stated above lead ores are frequently intermingled with zinc ores and concentration of the mixed material is carried out both by flotation and by wet gravity methods. Complete separation of the lead ore from the zinc is rarely attained in

practice by ore-dressing operations and the lead ore sent to the smelter may contain as much as 5 per cent zinc along with 75 per cent of lead.

Roasting. The concentrate from the concentration processes are then roasted in a reverberatory furnace. During roasting the sulphur content of the material is largely reduced and lead oxide is formed, thus—

$$2PbS + 3O_2 = 2PbO + 2SO_2 \uparrow$$

This material forms a sinter which is very suitable for charging into the blast furnace in the next stage of the extraction process.

Smelting. The roasted sinter along with coke (to serve both as fuel and reducing agent), iron, and limestone to act as a flux, are then charged into a blast furnace in which reduction to metallic lead occurs. The reactions involved during smelting are many, but the chief are as follows. The lead oxide is reduced by the carbon, and the unchanged lead sulphide by the iron—

(i) $$PbO + C = Pb + CO \uparrow$$

(ii) $$PbS + Fe = Pb + FeS$$

The products of the blast furnace are (*a*) crude lead, (*b*) matte and slag, and (*c*) fume and dust.

Refining of Lead. Lead contains two types of impurities, (i) base metals, and (ii) precious metals. In refining, both types are removed. Two processes are employed for the refining of crude lead; they are—

(*a*) *Fire-refining* in which molten lead from the blast furnace is retained in the molten condition in a drossing kettle and "poled" by mechanically agitating the molten lead by means of compressed air or by steam. The base metal impurities rise to the surface as oxides and are removed by skimming with a perforated disc or spoon. Other fire-refining processes are the Parke's and Luce Rozan processes (*see* pp. 469, 470).

(*b*) *Electrolytic refining* is carried out by the Betts process (*see* p. 471).

Physical Properties of Lead

(*a*) Lead exhibits a bluish-grey colour, and on a clean surface shows a metallic lustre.

(*b*) It is the softest of the metals in common use, it flows readily under pressure, and can be pressed into any form and extruded as rod and pipe.

(*c*) It is very malleable and can be readily rolled into thin sheets (lead foil); owing to its low strength, however, it cannot be drawn into wire.

(*d*) It is the heaviest of the common metals, its density being 11·34 g/cm^3.

(*e*) It has a low melting point (327·4°C); it boils at 1744°C, but is appreciably volatile at much lower temperatures than the boiling point and there is always loss on melting.

(*f*) It is a poor conductor of electricity and heat, being about 7 for the former and 8 for the latter, on scales having silver 100.

Chemical Properties of Lead

(*a*) On exposure to the air, lead is rapidly tarnished owing to the formation of a superficial layer of the white hydroxide and the carbonate; this film inhibits further attack to a large extent and accounts for the corrosion resistance of the metal.

(*b*) Pure air-free water does not attack lead, but the presence of dissolved air results in solution of the metal owing to the formation of the slightly-soluble plumbous hydroxide. Thus natural waters which have been softened to a low degree of hardness should not be circulated through lead pipes or the dissolved lead hydroxide may lead to poisoning. If such natural water, however, contains dissolved sulphate or carbonate the attack of the water is inhibited owing to the formation of a protective layer of lead carbonate and/or sulphate.

(*c*) When lead is heated in the air it slowly reacts to form lead monoxide, PbO (litharge). Further heating converts litharge into red lead, Pb_3O_4.

(*d*) Lead combines directly with chlorine to form lead chloride, $PbCl_2$; and with sulphur to form lead sulphide, PbS. It combines directly both with carbon and with nitrogen.

(*e*) Lead is only attacked slowly by hydrochloric acid, whether dilute or concentrated.

Dilute sulphuric acid likewise has no appreciable action upon lead. Hot concentrated sulphuric acid reacts with the metal to form lead sulphate and liberate sulphur dioxide, thus—

$$Pb + 2H_2SO_4 = PbSO_4 + 2H_2O + SO_2 \uparrow$$

With nitric acid, lead reacts to form lead nitrate (plumbous nitrate), $Pb(NO_3)_2$, and evolve oxides of nitrogen.

In the presence of air, lead is attacked by weak organic acids such as acetic acid and carbonic acid.

(*f*) Lead is not attacked by alkalis.

Uses of Lead. Lead is used for building purposes in the form of sheet and pipe. Lead sheet is also used for the lining of containers for dehydrated food. Lead is also used in the chemical industry for the lining of many types of reaction vessels and as a material for making the sheaths of electric cables.

The metal is also used as raw material for the manufacture of many types of lead compound such as lead azide, which often replaces mercury fulminate as a detonator, and lead tetraethyl used in aviation petrol. Lead is often used as an anti-corrosion coating for steel, to replace galvanizing; such lead coatings may be applied either by hot-dipping or by electroplating.

Lead is also an important constituent in many important alloys, for example soft solders, type metal and Wood's metal (*see* p. 710), white metals for bearings (28–80 per cent Pb: 5–93 per cent Sn: 4–15 per cent Sb: 1·5–3·5 per cent Cu), for accumulator plates (92 per cent Pb: 8 per

cent Sb), and lead bronzes (8·0–35·0 per cent Pb: 5·0–10·0 per cent Sn: 0·5–1·0 per cent Ni: 0·05–0·3 per cent P: copper making up the balance).

Compounds of Lead

Lead forms two series of compounds, the plumbous compounds and the plumbic compounds, the former being divalent and the latter tetravalent.

Plumbous Oxide, PbO, or lead monoxide is formed as a yellow powder when metallic lead is heated gently in air. This dross is known as *massicot*. When this massicot is heated and the mass powdered an orange-yellow variety of the monoxide is obtained; this is termed *litharge*.

Properties of Plumbous Oxide. Lead monoxide dissolves slightly in water to give an alkaline solution of plumbous hydroxide, $Pb(OH)_2$. The monoxide is amphoteric, reacting with acids to form the corresponding plumbous salts, and with caustic alkalis to form soluble plumbites, lead hydroxide being precipitated initially.

(i) $$PbO + 2HCl = PbCl_2 + H_2O$$

(ii) $$PbO + 2NaOH = Na_2PbO_2 + H_2O$$

Lead monoxide is readily reduced to metal by heating with the usual reducing agents such as the following—

(i) $$PbO + H_2 = Pb + H_2O \uparrow$$

(ii) $$PbO + C = Pb + CO \uparrow$$

(iii) $$PbO + CO = Pb + CO_2 \uparrow$$

(iv) $$PbO + KCN = Pb + KCNO$$

Uses of Plumbous Oxide. Lead monoxide is principally used for filling the grids of electrical storage battery plates, in the manufacture of flint glass, frits for earthenware glazes, for the production of lead acetate and nitrate, for driers for paint and varnish, for proofing fabrics, and the manufacture of certain rubber goods, linoleum, lead plaster and some insecticides. For use in the manufacture of glass, lead monoxide should only contain traces of iron, copper and silver.

Red Lead, Pb_3O_4 (Triplumbic tetroxide or Minimum). On a commercial scale red lead is made by heating lead monoxide in a furnace at a temperature not exceeding 460°C. The monoxide is oxidized as follows—

$$6PbO + O_2 \rightleftharpoons_{460°C} 2Pb_3O_4$$

At temperatures in excess of 460°C, the reverse reaction occurs and the monoxide is re-formed. The proportion of red lead in the product may be varied at will; the higher ranges (over 93·15 per cent Pb_3O_4) do not set with linseed oil and are therefore suitable for use in ready-mixed paints.

Properties of Red Lead. In its chemical reactions red lead behaves as though its constitution is $2PbO \cdot PbO_2$. Thus when it reacts with hot

dilute nitric acid it forms a solution of plumbous nitrate and a precipitate of lead dioxide—

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2\downarrow + 2H_2O$$

With hydrochloric acid, lead chloride is formed and chlorine is liberated. It is not unlikely that lead dioxide is formed as an intermediary product, thus—

(i) $$Pb_3O_4 + 4HCl = PbCl_2 + PbO_2\downarrow + 2H_2O$$

(ii) $$PbO_2 + 4HCl = PbCl_2 + Cl_2\uparrow + 2H_2O$$

Uses of Red Lead. About 60 per cent of the world production of red lead is used in pasting the plates of electric storage batteries, whilst about 30 per cent is used for paint, mostly for protecting iron and steel. Other uses include its employment for the manufacture of flint and optical glass, in some pottery glazes, match-making, jointing compositions, and in the manufacture of driers for varnish.

Orange lead, a variety of red lead produced by the calcination of white lead, and containing upwards of 95 per cent true red lead, has a low bulk density and less tendency than has ordinary red lead to set in paint media containing varnish. It is a valuable pigment for use in printing inks, in certain enamels and in lakes.

Lead Carbonate, $PbCO_3$. In the laboratory, lead carbonate may be prepared by the addition of a solution of sodium bicarbonate to the aqueous solution of a lead salt.

$$Pb^{++} + 2(HCO_3)' = PbCO_3\downarrow + H_2O + CO_2$$

The addition of sodium carbonate solution gives rise to the formation of basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$. This compound, which is also known as *white lead*, is an exceedingly important lead pigment; it is made on a large scale by two processes, namely, the older "Dutch process," and the more recent "Carter process."

In the Dutch process, lead is melted and cast into the form of 6 in. disks. These are placed on shelves in small earthenware pots containing 3 per cent acetic acid in vessels underneath the shelves. The pots are stacked in tiers and spent tannery bark placed all round them, the reaction vessels being then sealed off, and left untouched for about 3 months. During this period the acetic acid vapour, moisture, and carbon dioxide from the fermentation of the tannery bark all act upon the lead and convert it into flaky white lead. This is then broken away from any unchanged lead, ground, floated in water and finally dried to give a product which contains about 70 per cent $PbCO_3$ and 30 per cent $Pb(OH)_2$.

In the Carter process, melted lead is atomized by spraying from nozzles by means of compressed air or steam. The finely divided lead is "corroded" with a spray of acetic acid, carbon dioxide and air in a large rotary furnace.

The Carter process occupies a time of 5–12 days and gives a material which is whiter, finer, and more uniform than that obtained by the Dutch process. The reactions for both the Dutch process and the Carter process are the same—

(i) $2Pb + O_2 = 2PbO$

(ii) $PbO + 2CH_3COOH = Pb(CH_3COO)_2 + H_2O$

(iii) $Pb(CH_3COO)_2 + 2PbO + 2H_2O = [Pb(CH_3COO)_2 . 2Pb(OH)_2]$

(iv) $3[Pb(CH_3COO)_2 . 2Pb(OH)_2] + 4CO_2 =$
$2[2PbCO_3 . Pb(OH)_2] + 3Pb(CH_3COO)_3 + 4H_2O$

White lead is one of the oldest and one of the most important of the white pigments. Paints made from this material have a high covering power and are very easily applied. They have the disadvantage, however, that they react readily with hydrogen sulphide forming black lead sulphide.

Lead Sulphate, $PbSO_4$, may be prepared by adding dilute sulphuric acid to the solution of a plumbous salt. It is a white compound which is only slightly soluble in water. *Basic lead sulphate* $PbO . PbSO_4$ finds application as a pigment.

The Lead Accumulator consists of a group of negative plates composed of finely-divided lead contained within a lead grid, and a group of positive plates containing a paste of lead dioxide also confined within a lead grid. The two groups of plates intermesh but do not touch one another. This composite block of positive and negative plates is immersed in an electrolyte of sulphuric acid.

When the positive plates are connected externally to the negative plates, an electric current flows through the circuit established and concurrently the following chemical reaction occurs—

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{Charging reaction}\leftarrow}{\overset{\text{Discharging reaction}\rightarrow}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$

On charging the reverse reaction occurs.

It will be noted that discharging is associated with dilution of the sulphuric acid (since water is produced by the reaction); it is therefore usual to control the degree of discharge of these cells by observation of the density of the sulphuric acid electrolyte, and when a certain minimum density is reached the cell is re-charged. If the discharging reaction is allowed to proceed to completion the lead sulphate formed in masses on the plates is very difficult to remove and the cells are said to be "sulphated."

Lead Chromate, $PbCrO_4$, is precipitated as a yellow solid when the aqueous solution of a soluble chromate is added to the solution of a lead

salt. It is employed as a yellow pigment under the names of *chrome yellow*, *lemon chrome* and *Cologne yellow*; if the chromate is boiled with alkali hydroxide solution it is converted into a red *basic lead chromate*, $PbCrO_4 . Pb(OH)_2$ which also finds application as a pigment, under the name of *chrome red.*

Lead Acetate, $Pb(CH_3COO)_2$, also known as *sugar of lead* is made by boiling litharge with acetic acid; the salt is obtained by evaporation of the solution. Lead acetate finds application in medicine and as a mordant.

Lead Dioxide, PbO_2, is prepared by the action of nitric acid on red lead.

$$\underbrace{2PbO . PbO_2}_{Pb_3O_4} + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 \downarrow + 2H_2O$$

Lead dioxide is precipitated as a dark chocolate coloured substance whilst the plumbous nitrate remains in solution; the former is then filtered off, washed with water and dried at 100°C.

It is also formed on the positive plate when a solution of a lead salt in sulphuric acid is electrolyzed (*see* Lead Accumulator, p. 624).

Properties of Lead Dioxide. When heated, lead dioxide decomposes above 300°C as follows—

$$2PbO_2 = 2PbO + O_2 \uparrow$$

It is insoluble in water, in nitric acid and in dilute hydrochloric and sulphuric acids. Concentrated hydrochloric acid reacts with it to form plumbous chloride and evolve chlorine, whilst concentrated sulphuric acid reacts to form plumbous sulphate and evolve oxygen.

With concentrated aqueous solutions of the alkali metals, lead dioxide reacts to form the corresponding plumbates, thus—

$$PbO_2 + 2NaOH = Na_2PbO_3 + H_2O$$

Lead dioxide is a powerful oxidizing agent, for example it reacts very vigorously with sulphur dioxide forming plumbous sulphate; the lead dioxide glows during this oxidation.

Lead dioxide is an amphoteric oxide owing to its ability to react with both acids and with alkalis.

Plumbic Tetrachloride, $PbCl_4$, is an oily yellow liquid of high density which is prepared by the action of concentrated sulphuric acid upon ammonium plumbichloride, thus—

$$(NH_4)_2PbCl_6 + H_2SO_4 = (NH_4)_2SO_4 + 2HCl + PbCl_4$$

Lead tetrachloride is decomposed on heating into plumbous chloride and chlorine—

$$PbCl_4 = PbCl_2 + Cl_2 \uparrow$$

Reaction with water gives rise to the formation of lead dioxide and hydrochloric acid—

$$PbCl_4 + 2H_2O = PbO_2 \downarrow + 4HCl$$

Lead Tetraethyl, $Pb(C_2H_5)_4$, is made by the reaction of plumbous chloride with magnesium ethyl iodide. Lead tetraethyl behaves as a negative catalyst when added to certain types of petrol to inhibit the tendency for pre-ignition.

CHAPTER 23

THE ELEMENTS OF GROUP V

NITROGEN is the first element of the Group V family—

Nitrogen—Phosphorus—Vanadium—Niobium—Tantalum (Group V*a*)

Nitrogen—Phosphorus—Arsenic—Antimony—Bismuth (Group V*b*)

Nitrogen and phosphorus are non-metals, vanadium, niobium and tantalum are metals, but the Group V*b* elements, arsenic, antimony and bismuth have characteristics of both and are sometimes referred to as metalloids. The principal valencies are three and five.

NITROGEN

Nitrogen forms the major constituent of the atmosphere, being present to the extent of about 79 per cent by volume or 76 per cent by weight. In chemical combination with other elements it occurs as sodium nitrate in Chile saltpetre, in proteins, and many other animal and vegetable products.

Preparation. Commercially, nitrogen is obtained almost exclusively from air by the process discussed in detail on pp. 381–384. The air is first liquefied and then fractionally evaporated so as to isolate, in a relatively pure form, not only nitrogen and oxygen but also the inert gases (neon, argon, etc.) which are present to a small extent in the atmosphere.

Some nitrogen is obtained commercially from air by burning out the oxygen with waste hydrogen, the latter for example being obtained as a by-product in the electrolysis of aqueous sodium chloride.

In the laboratory, nitrogen (together with the inert gases) may be prepared from air by passing the latter successively through—

(i) a strong solution of sodium hydroxide, to remove any acidic gases, such as carbon dioxide and sulphur dioxide, and

(ii) an alkaline solution of pyrogallol; or slowly over strongly heated copper turnings contained, for example, in a hard glass tube, to remove the oxygen.

The residual nitrogen may then be collected over water, but note that it will still contain the inert gases. If required pure, the nitrogen is first converted into magnesium nitride, Mg_3N_2, by strongly heating magnesium in the gas. Ammonia is then liberated by the action of water, and the ammonia then passed over heated copper oxide to liberate the nitrogen.

Chemically pure nitrogen is however best prepared in the laboratory from nitrogen-containing compounds by one of the following methods—

(*a*) By the thermal decomposition of ammonium nitrite—

$$NH_4NO_2 = 2H_2O + N_2$$

In practice, since this reaction may occur explosively, it is safer to heat a mixture of solutions of ammonium chloride and sodium nitrite. The ammonium nitrite then decomposes as it is formed from these two reactants—

$$NH_4Cl + NaNO_2 = NaCl + 2H_2O + N_2$$

The gas is then bubbled through sodium hydroxide solution to remove traces of free chlorine, through concentrated sulphuric acid to remove any free ammonia and to dry the gas, and finally over heated copper turnings to decompose any oxides of nitrogen present.

(*b*) By heating ammonium dichromate (or a mixture of ammonium chloride and potassium dichromate) followed by purification as in (*a*).

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$$

(*c*) From ammonia, either by passing the gas over heated copper oxide

$$3CuO + 2NH_3 = 3Cu + 3H_2O + N_2$$

or less satisfactorily by the action of chlorine on ammonium hydroxide (but excess of chlorine gives the explosive nitrogen trichloride NCl_3), the hydrogen chloride dissolving in the water present—

$$2NH_3 + 3Cl_2 = 6HCl + N_2$$

(*d*) From the various oxides of nitrogen by passing these gases over heated copper turnings—

$$2Cu + 2NO = 2CuO + N_2$$

(*e*) From urea by oxidation with aqueous sodium hypochlorite, NaClO or with nitrous acid—

$$CO(NH_2)_2 + 3NaOCl + 2NaOH = Na_2CO_3 + 3NaCl + N_2 + 3H_2O$$

$$CO(NH_2)_2 + 2HNO_2 = H_2CO_3 + 2N_2 + 2H_2O$$

Physical Properties of Nitrogen. A colourless, odourless gas, slightly soluble in water (but less so than oxygen), it may be liquefied at −195°C and solidified at−214°C. It is not poisonous, but does not support life. In the absence of oxygen, animals are suffocated; they are not poisoned by the nitrogen. Cylinders of nitrogen are available commercially in grey coloured cylinders, the top (or shoulder) of which is painted black.

Chemical Properties of Nitrogen. Nitrogen is often loosely regarded as a non-reactive element, a view which is based on its general non-reactivity when compared with oxygen at moderate temperatures up to about 200°C.

It will be recalled that oxygen might similarly be regarded as non-reactive if its reactivity at room temperatures only were considered. The fact is that the nitrogen molecule is more stable than the oxygen molecule, so that a higher temperature is necessary before sufficient partial dissociation occurs to initiate chemical reaction. If the resulting reaction then occurs with further evolution of heat, that is, is exothermic, then further dissociation of nitrogen molecules will occur and the nitrogen reacts.

The molecular structure of nitrogen contains three covalent linkages between the two nitrogen atoms, N≡N, whereas oxygen contains only two, O=O, and fluorine one, F—F. Of these three gases, fluorine is extremely reactive even at ordinary temperatures, oxygen in general requires moderate heating, whilst nitrogen requires considerable heating before reaction occurs. It appears that the reactivity of these gases is inversely proportional to the number of covalent linkages involved in the respective molecules, with nitrogen consequently the least reactive. This conclusion is supported by measurements of the heats of dissociation of nitrogen, oxygen, and fluorine. These are found to be approximately in the ratio of 3:2:1—

$$N_2 = 2N - 169{\cdot}3 \text{ cal.}$$
$$O_2 = 2O - 117{\cdot}4 \text{ cal.}$$
$$F_2 = 2F - 64{\cdot}0 \text{ cal.}$$

The chemical reactivity of nitrogen is revealed by such reactions as—

(i) It combines with many metals on heating to a dull red heat or higher temperature to form *nitrides*. Thus, when magnesium is burnt in air, it forms not only magnesium oxide but also the pale yellow magnesium nitride, Mg_3N_2. The presence of the latter may readily be detected by moistening the solid with water to liberate the easily recognizable ammonia gas—

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

Lithium, calcium and boron also burn when heated strongly in nitrogen to form nitrides, Li_3N, Ca_3N_2 and BN.

(ii) It combines with most non-metals at sufficiently elevated temperatures. Thus reaction with oxygen occurs to a small extent above 1000°C to form nitric oxide, the yield of which is increased to about 5 per cent at 3000°C (*see* Arc Process, p. 631). Ammonia gas is formed when nitrogen and hydrogen react together at 400–600°C, a reaction which is the basis of the modern industrial processes for synthesizing ammonia and hence nitric acid, etc. (*see* Haber Process, p. 634). Nitrogen also combines at high temperatures with carbon, silicon and boron.

(iii) It combines directly with calcium carbide at about 1000°C to form calcium cyanamide, $CaCN_2$, an important nitrogenous fertilizer—

$$CaC_2 + N_2 = CaCN_2 + C$$

Uses of Nitrogen. The principal use of nitrogen is in the manufacture of ammonia from which nitrogenous fertilizers, nitric acid and related compounds, and urea are now mainly prepared. Smaller quantities are used to provide an inert atmosphere in certain metallurgical operations, in high temperature mercury-in-glass thermometers, etc.

The Nitrogen Cycle in Nature

It is no exaggeration to say that all forms of living matter, both animal and vegetable, require some form of chemically combined nitrogen for their sustenance. Thus plant-life depends upon the presence of nitrates and certain other nitrogenous compounds in the soil (although phosphates, potassium compounds, and traces of compounds of certain elements are also necessary), whilst animals require proteins, which are somewhat complex organic compounds containing nitrogen. The animals obtain their proteins from plants, and in the natural course of events return these and other nitrogenous compounds back to the soil in the form of excreta and the products of animal decay. Certain bacteria present in the soil convert these organic nitrogen compounds into other compounds, such as nitrates upon which plant-life depends, and thus the *nitrogen cycle* is completed.

This simple cycle is not however one hundred per cent efficient; a steady loss of nitrogen occurs from two causes. Thus, the bacteria in the soil convert only a part of the organic matter into nitrates, etc., and some free nitrogen is produced which escapes into the atmosphere. The second cause is a man-made one. The progress of civilization has resulted in improved methods of sanitation, with the result that enormous quantities of waste organic matter are now discharged into the rivers and seas or otherwise wasted.

Nature tends partially to restore the resultant drainage of nitrogen from the land by two distinct processes. Certain plants, known as the leguminosae (peas, beans, clover, etc.) are able to assimilate nitrogen directly by the action of certain bacteria present in nodules in the roots. The latter apparently convert the nitrogen into compounds suitable for plant-life. By growing a crop of clover, for example, after corn or wheat, the nitrogenous food matter in the soil is replenished and indeed so effective is this method for preserving the fertility of the soil that at Rothamsted the rotation of crops has been successfully carried out without artificial fertilization for a period of well over a hundred years. The second process whereby nature attempts to restore the balance of nitrogen in the soil occurs during electrical storms (lightning, etc.) and results in the formation of important quantities of nitric acid and hence of nitrates.

The need for ever-increasing quantities of cereals and other vegetable food-stuffs in the world of today has meant that the soil must be enriched

with nitrogen-containing compounds obtained from other sources if its productivity is to be maintained or even increased. For a long time the only sources of these compounds were—

(*a*) The extensive deposits of Chile saltpetre, $NaNO_3$ which occur in South America.

(*b*) The sulphate of ammonia, produced as a by-product in the purification of coal-gas in gas-works.

Nowadays, the greater part of the enormous world demand for nitrogenous fertilizers is obtained synthetically from atmospheric nitrogen, and the fear that with the exhaustion of the Chile nitrate-beds the supply of nitrogen fertilizers would necessarily diminish has thus been completely removed.

The processes whereby the inexhaustible supplies of nitrogen in the atmosphere may be converted, or "fixed," industrially into useful compounds began with the now mainly absolescent "Arc Process," which has almost entirely been replaced by the "Cyanamide" and the very important "Synthetic Ammonia" processes. The student will appreciate that the liquefaction and fractional distillation of air to separate more or less pure nitrogen does not in itself constitute a "fixation" of the nitrogen, and that the latter in its elementary form is not a food-stuff.

Fixation of Atmospheric Nitrogen

The Arc Process. Priestley first noticed that a decrease in volume occurs when an electric spark is passed through air confined over water, and that the latter becomes acidic. In 1780, Cavendish repeated the experiment and found that nitrites and nitrates were formed if sodium hydroxide solution replaced the water. The development of cheap hydro-electric power in Norway led in 1904 to the development of the Birkeland-Eyde Process, and the manufacture of considerable quantities of calcium nitrate fertilizers.

The process is based on the reversible and highly endothermic reaction—

$$N_2 + O_2 \rightleftharpoons 2NO - 43\,200 \text{ cal.}$$

nitric oxide

By applying Le Chatelier's Principle, it is seen that the equilibrium yield of nitric oxide may be increased by increasing the temperature of the reaction. No appreciable reaction however occurs below 1000°C, and even at this temperature the equilibrium yield is less than a half of one per cent. At about 3000°C, the yield is increased to about five per cent. This temperature is produced in practice by a powerful electric arc. The latter is drawn out, by means of suitably arranged powerful electro-magnets, into a large alternating disc of flame in a flat circular furnace and air is blown rapidly through the flame.

The main problem, however, is to "fix" this small yield of nitric oxide. If the temperature of the issuing air is not reduced very rapidly to well below 1000°C (in order to slow up the rate at which the forward and back reactions involved in the above equilibrium occur) the equilibrium yield of the nitric oxide automatically reduces itself with the falling temperatures, and the benefit of the initial high temperature reactions will be lost. In practice, therefore, the air containing the nitric oxide is rapidly cooled by passing successively through brick-lined iron pipes, steel boilers, and aluminium pipes, but even then the resultant yield of nitric oxide is little more than one per cent. The cumulative nature of the process and the

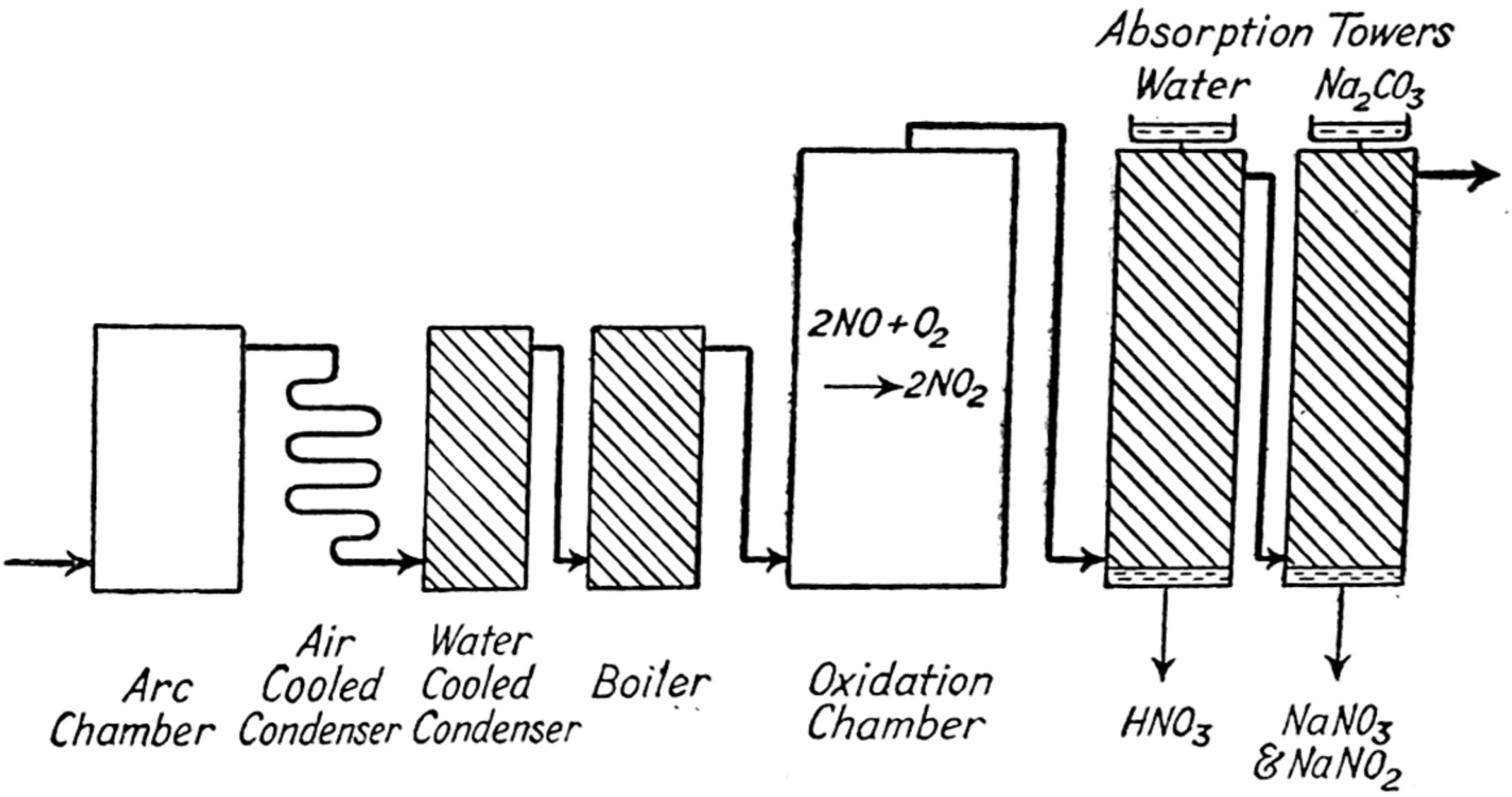


FIG. 200. Manufacture of Nitric Acid by the Arc Process

fact that the air costs nothing makes even this relatively small conversion one of considerable importance.

Below about 600°C, the nitric oxide then begins to combine with more oxygen to form nitrogen peroxide by the reaction—

$$2NO + O_2 \rightleftharpoons 2NO_2$$

This reaction is also reversible, and occurs more completely the lower the temperature. To allow time for the relatively slow conversion of the nitric oxide to nitrogen peroxide, the air containing the nitric oxide is passed through large empty iron-towers on their way to the absorption towers. These latter consist of large towers some 80 ft high and filled with broken quartz down which a stream of water is passed. The air enters near the base of the tower and the nitrogen peroxide is removed by such reactions as—

$$2NO_2 + H_2O = HNO_2 + HNO_3$$

More nitric acid forms as a result of the decomposition of the nitrous acid and further oxidation of the liberated nitric oxide—

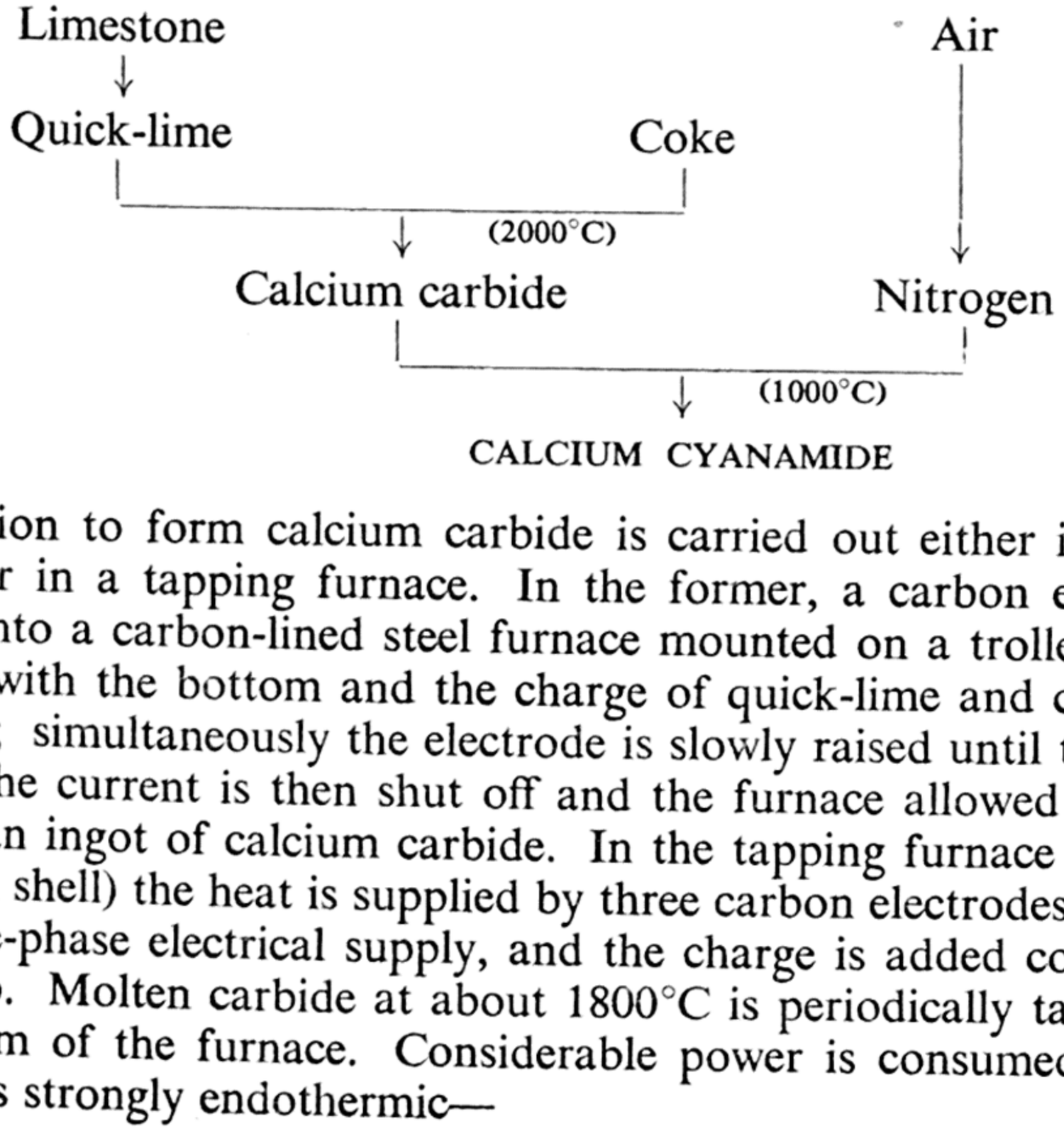
$$3HNO_2 = 2NO + HNO_3 + H_2O$$
$$2NO + O_2 = 2NO_2$$

Any remaining oxides of nitrogen are removed by washing the air with aqueous sodium carbonate in further absorption towers to form sodium nitrite.

The process thus "fixes" atmospheric nitrogen in the form of nitric acid and sodium nitrite. The nitric acid is about 30 per cent concentrated, and in times of peace is mostly neutralized with limestone to form calcium nitrate, which is used extensively as a fertilizer.

The Cyanamide Process. The Cyanamide process has as its starting materials limestone, coke and air. Quick-lime, CaO, is produced from limestone, $CaCO_3$, by the usual lime-kiln process (*see* p. 502), and is then converted into calcium carbide, CaC_2, by heating with coke at about 2000°C. Relatively pure nitrogen, obtained from air by the liquefaction and fractional evaporation process (*see* p. 381), then reacts with the carbide at about 1000°C to form calcium cyanamide, $CaCN_2$—

$$CaC_2 + N_2 = CaCN_2 + C$$



The reaction to form calcium carbide is carried out either in an ingot furnace or in a tapping furnace. In the former, a carbon electrode is lowered into a carbon-lined steel furnace mounted on a trolley. An arc is struck with the bottom and the charge of quick-lime and coke added gradually; simultaneously the electrode is slowly raised until the furnace is full. The current is then shut off and the furnace allowed to cool to produce an ingot of calcium carbide. In the tapping furnace (a carbon-lined steel shell) the heat is supplied by three carbon electrodes connected to a three-phase electrical supply, and the charge is added continuously at the top. Molten carbide at about 1800°C is periodically tapped from the bottom of the furnace. Considerable power is consumed since the reaction is strongly endothermic—

$$CaO + 3C = CaC_2 + CO\uparrow - 103\,000 \text{ cal.}$$

The conversion of the carbide to cyanamide is carried out at about 1000°C in fire-brick lined steel vessels. A central carbon rod serves as an electrical resistance element to provide sufficient heat to initiate the reaction—

$$CaC_2 + N_2 = CaCN_2 + C + 68\,000 \text{ cal.}$$

Nitrogen, obtained as described above from the air, is admitted near the base of the vessel. The heat of the reaction is sufficient to maintain the temperature at about 1000°C, without further electrical heating. After a time, varying from one to two days depending upon the amount of the charge, the reaction is complete, and the calcium carbide is obtained as a black powder. This is sprayed with water to decompose any unchanged carbide and slake any residual lime.

$$CaC_2 + 2H_2O = Ca(OH)_2 + \underset{\text{acetylene}}{C_2H_2}\uparrow$$

Calcium cyanamide is used extensively as a nitrogenous fertilizer. Smaller quantities are used to prepare sodium cyanides and ferrocyanides by reactions, such as—

$$CaCN_2 + 2NaCl + C \xrightarrow{\text{fuse}} CaCl_2 + 2NaCN$$

$$6NaCN + FeSO_4 + CaCl_2 + 2H_2O \rightarrow CaSO_4 . 2H_2O + Na_4[Fe(CN)_6] + 2NaCl$$

Free ammonia may also be obtained by treating the cyanamide with superheated steam in closed reaction vessels, known as autoclaves—

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3\uparrow$$

"Synthetic" Ammonia (Haber Process). By far the greatest proportion of the world's production of ammonia (and hence, of nitric acid and nitrates) is obtained by the direct combination of nitrogen and hydrogen—

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 25\,000 \text{ cal.}$$

By applying Le Chatelier's principle to this reversible reaction, it is seen that the equilibrium yield of ammonia should be increased—

(*a*) by reducing the temperature—since the reaction is exothermic,
(*b*) by increasing the pressure—since the reaction to produce the ammonia is accompanied by a reduction in volume.

For the process to be economically successful, however, a third factor must be considered, namely, the time required for the reaction to reach the equilibrium state. Lowering the temperature increases the equilibrium yield of ammonia but also considerably increases the time required to reach this equilibrium state. The increased percentage conversion of the nitrogen and hydrogen to ammonia would clearly not justify this enormous

increase in time, unless other means to reduce this time factor can be found. The solution is found in the use of a suitable catalyst.

It will be recalled that a catalyst is a substance which speeds up the rate of both the forward and back reactions of a reversible reaction by the same amount (so that the position of equilibrium is unchanged) and is itself chemically unchanged. The best catalyst for the process has been found to be metallic iron containing small amounts of both an amphoteric oxide such as alumina or silica and an alkaline oxide such as potassium oxide. Since these catalysts are rapidly poisoned, particularly by such substances as sulphur, arsenic and phosphorus, it is important that the

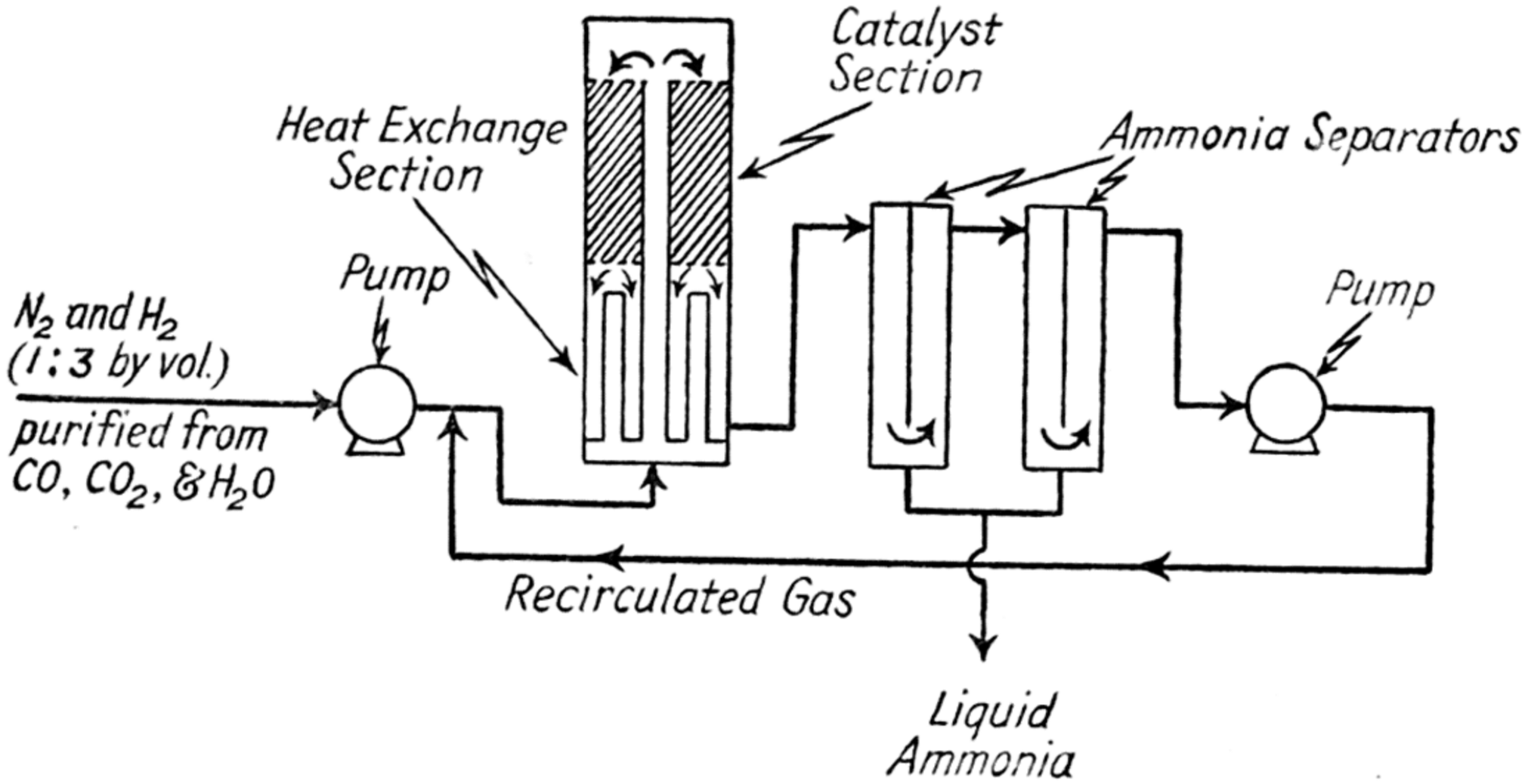


FIG. 201. Synthesis of Ammonia

hydrogen and nitrogen be thoroughly purified if the efficiency of the process is to be maintained.

The hydrogen is obtained by one or other of the commercial processes described on pp. 366–368, depending upon the locality of the plant. The nitrogen is obtained from the atmosphere, either by the liquefaction and fractional evaporation process (*see* p. 381), or from producer gas by removing the carbon monoxide and carbon dioxide. Or, the mixture of hydrogen and nitrogen may be prepared directly from water-gas by the Bosch process (*see* p. 367). The mixture of hydrogen and nitrogen, in the ratio of three to one by volume, is then compressed in the Haber Process to 200 atmospheres pressure and passed over the catalyst maintained at about 550°C. The exothermic nature of the reaction supplies sufficient heat to maintain the catalyst at this temperature, provided that the loss of heat is reduced to a minimum. The hot gases leaving the catalyst-bomb accordingly pass through a heat interchanger in order to preheat the incoming hydrogen-nitrogen mixture. As the percentage conversion to ammonia is only about 5–10 per cent, the residual gases obtained after

washing out the ammonia, or removing it as the liquid, are mixed with more hydrogen and nitrogen and again passed through the catalyst, so that ultimately a practically one hundred per cent conversion to ammonia is obtained.

The conditions under which the process is carried out varies in different parts of the world. Thus, in the *Claude modification*, the reaction is carried out at about 1000 atmospheres pressure at a catalyst temperature of between 500 to 650°C, to give a 40 per cent conversion to ammonia. By using several converters in series, the yield is further increased to about 85 per cent. The ammonia is removed as the liquid, and the residual gases allowed to escape.

The ammonia produced by these processes is very pure, and is the intermediate in the chief present-day process for the manufacture of nitric acid and nitrates. For fertilizer use, it may be converted into ammonium sulphate by the double decomposition reaction with carbon dioxide and calcium sulphate, described on p. 638.

To recapitulate, the drainage of nitrogen from the soil results from the harvesting of crops, from the consumption of vegetable matter by animals, and also from the leaching action of water which dissolves the soluble nitrogenous compounds. These losses are partially compensated by bacterial fixation of nitrogen (leguminosae), by appreciable fixation of nitrogen during electrical storms, and by the application of nitrogenous fertilizers obtained either from naturally occurring nitrates (Chile saltpetre) or by one or other of the processes for fixing atmospheric nitrogen described in detail above. The practical success of these latter fixation processes has removed the fear that with the working out of the natural nitrate beds the flow of nitrogenous fertilizers to the soil would gradually cease, with the result that the natural fertility of the soil would steadily decrease and less and less food-stuffs be produced.

Compounds of Nitrogen

Hydrides. These include the very important compound, ammonia, and also hydrazine and hydrazoic acid.

Ammonia, NH_3. The usual laboratory method of preparation is to heat a solid mixture of ammonium chloride and soda-lime (quick-lime slaked with sodium hydroxide solution)—

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O$$

Aqueous sodium hydroxide may also be used in place of the soda-lime, but it would then be necessary to boil the solution to expel the very soluble ammonia. The ammonia gas is dried by passing up a tower filled with quick-lime and collected by downward displacement of air.

Ammonia is formed quantitatively by the reduction of nitrates and

nitrites with Devarda's Alloy (Al, 45: Cu, 50: Zn, 5) and sulphuric acid. The ammonia reacts with the excess of acid to form ammonium sulphate and may be liberated as above by adding excess of sodium hydroxide and boiling—

$$HNO_3 + 8\overline{H} = NH_3 \uparrow + 3H_2O$$

nascent

This reduction, although rarely used as a method of producing ammonia, is one of the standard methods for estimating a nitrate. The ammonia liberated is absorbed in a known volume of standard acid, and the residual acid then determined by back titration.

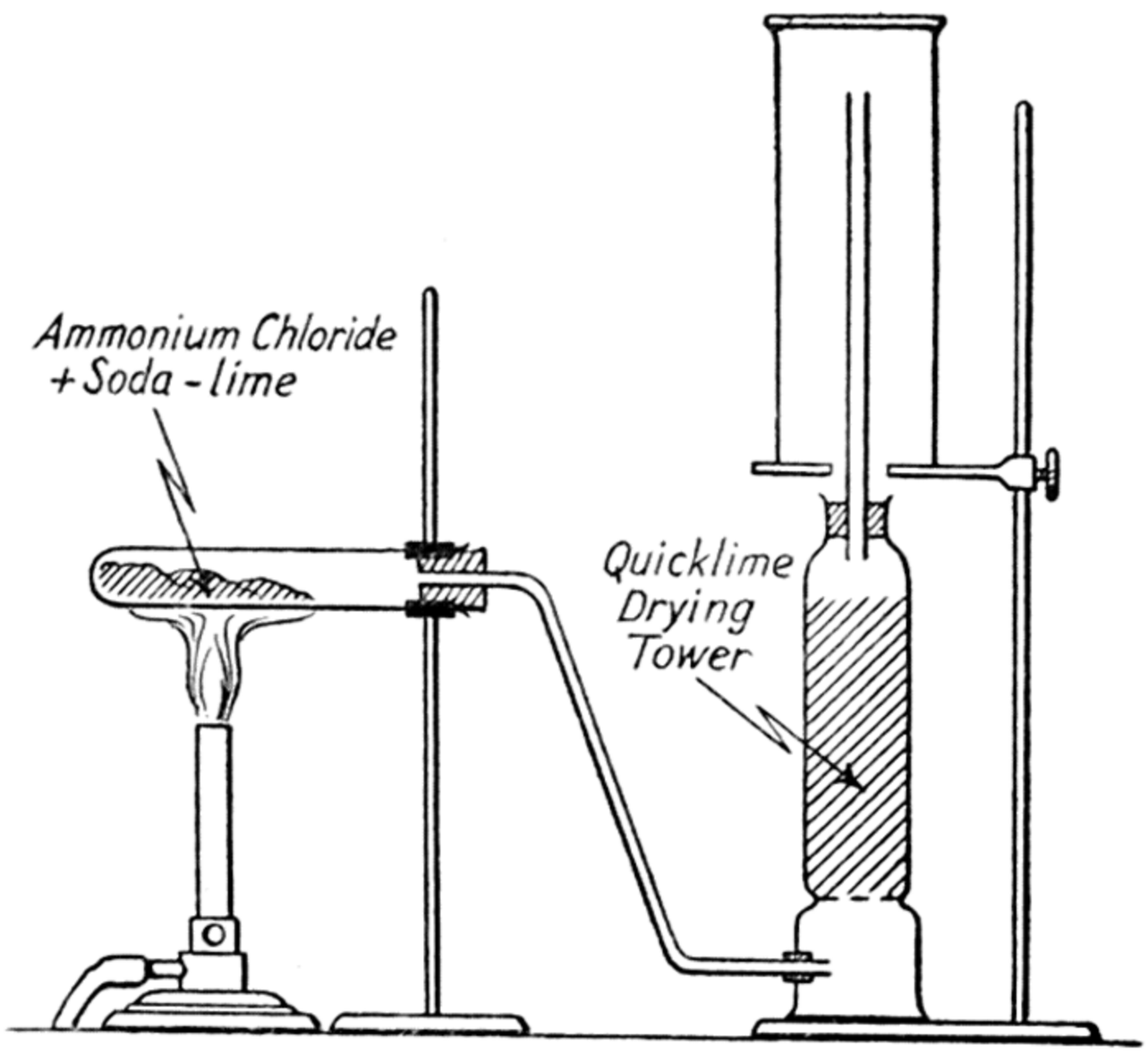


FIG. 202. Preparation of Ammonia

Ammonia is liberated by the action of water on certain nitrides, such as those of magnesium and calcium. Boron nitride and calcium cyanamide both require superheated steam—

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3 \uparrow$$

$$BN + 3H_2O = H_3BO_3 + NH_3 \uparrow$$

boric acid

Certain ammonium salts also liberate ammonia when heated strongly. The principal exceptions appear to be the ammonium salts of the stronger oxidizing acids. Thus ammonium dichromate liberates nitrogen, ammonium nitrate liberates nitrous oxide, and ammonium nitrite liberates nitrogen.

Commercial Preparations of Ammonia. These may be divided into two categories, (*a*) by-product ammonia and (*b*) synthetic ammonia.

(*a*) *By-product Ammonia.* Considerable quantities of ammonia are

produced in the gasification of coal (*see* p. 587). This ammonia is recovered as ammonium sulphate ("sulphate of ammonia") either by neutralizing the ammoniacal liquor with sulphuric acid, or by a double decomposition reaction with carbon dioxide and a suspension of very fine calcium sulphate (in the form of gypsum)—

$$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + CaSO_4 = CaCO_3\downarrow + (NH_4)_2SO_4$$

Formerly, an aqueous solution of ammonia, known as *spirits of hartshorn*, was obtained by distilling waste animal hides and hoofs, etc.

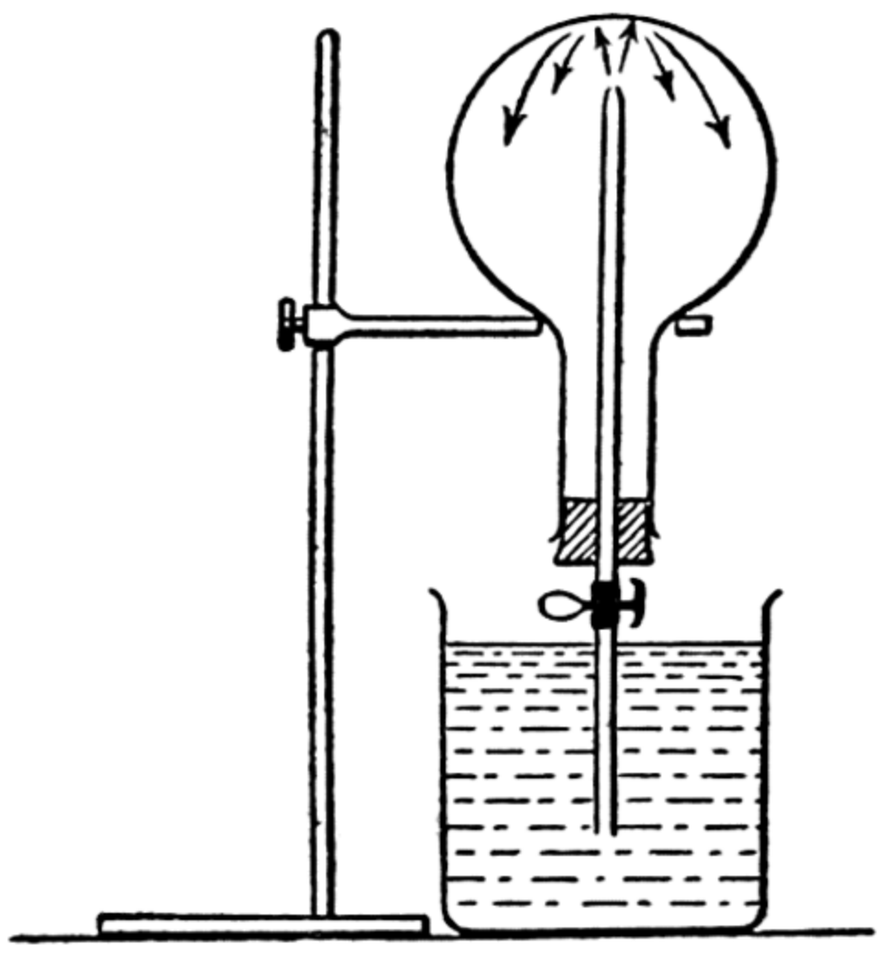


FIG. 203. Fountain Experiment

(*b*) *Synthetic Ammonia.* The production of ammonia directly from hydrogen and nitrogen has already been fully described in connexion with the fixation of atmospheric nitrogen (*see* p. 634). This process provides the bulk of the world's supplies of ammonia, and hence of nitric acid and nitrates. The manufacture of nitric acid from synthetic ammonia will be discussed later in connexion with this acid. The production of ammonia by treating calcium cyanamide with super heated steam in autoclaves is nowadays relatively unimportant, the bulk of the cyanamide being used directly as a nitrogenous fertilizer.

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3\uparrow$$

Physical Properties of Ammonia. Ammonia is a colourless gas with a pungent odour. It is lighter than air (8·5, cf. 14·4), and is extremely soluble in water (1300 vol in one volume of water at°0 C and 760 mm). This considerable solubility is often demonstrated in the laboratory by the so-called "fountain experiment," as illustrated in the accompanying diagram. The glass vessel is filled with dry ammonia gas and the apparatus arranged as shown. By gently warming the bulb and then allowing it to cool, a little water is drawn up the capillary tube and discharges into the flask. There, it immediately dissolves practically the whole of the ammonia gas to create a partial vacuum. The vigorous inrush of water up the capillary-tube which results, produces a fountain-like effect.

That the solubility of ammonia gas in water does not obey Henry's law is due to the additional reactions which occur—

$$\underset{\text{gas}}{NH_3} \rightleftharpoons \underset{\text{solution}}{NH_3}$$

$$\underset{\text{solution}}{NH_3} + H_2O \rightleftharpoons \underset{\substack{\text{ammonium}\\\text{hydroxide}}}{NH_4OH} \rightleftharpoons NH_4^+ + OH^-$$

Henry's Law deals only with the first equilibrium reaction however, and in fact calculations of the equilibrium concentration of the free ammonia molecules in solution show this to be in accordance with Henry's Law.

The strongest solution of ammonia available commercially is known as "0·880 Ammonia," the numerical prefix indicating the specific gravity of the solution. The higher the specific gravity the weaker the solution.

Ammonia is easily liquefied and solidified (— 33·5°C and — 78°C respectively at ordinary pressures). The boiling point may however be raised by increasing the pressure; for example it boils at 25°–26°C when the pressure is 10 atmospheres. This fact, coupled with the relatively high value of the latent heat of evaporation—

$$\underset{\text{liquid}}{NH_3} \rightarrow \underset{\text{gas}}{NH_3} - 5700 \text{ cal.}$$

accounts for its wide use in refrigeration plant. Liquid ammonia, under pressure in the cooling part of the plant, is allowed to evaporate through a reducing valve. The necessary latent heat of evaporation is absorbed from the surrounding cooling coils in which circulates a brine solution. The ammonia gas is recondensed by passing through a compression pump, and the liberated heat of condensation passed on to a cold water cooling coil system. Heat is thus abstracted from the brine solution and dissipated through the water coils.

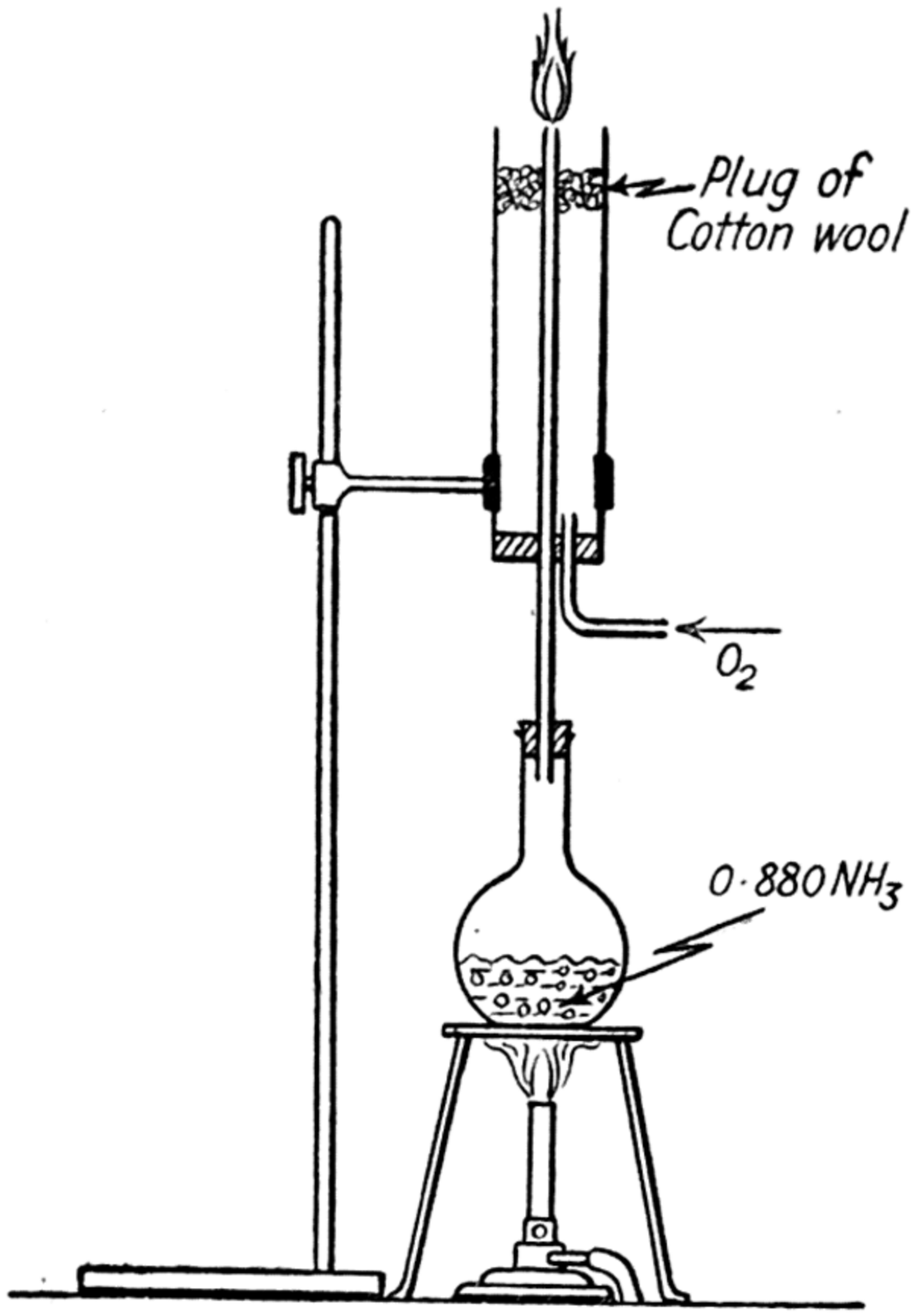


FIG. 204. Ammonia Burning in Oxygen

Chemical Properties of Ammonia. Ammonia does not support combustion nor burn in air. It will, however, burn with a peach coloured flame in an atmosphere of oxygen to form nitric oxide—

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

The same apparatus, shown in the accompanying diagram, may also be used to show oxygen burning in ammonia, simply by interchanging the gases. The oxidation of ammonia may also be carried out catalytically in presence of a heated platinum wire. Once the reaction starts, the heat

liberated is sufficient to maintain the temperature of the platinum wire; by increasing the proportion of oxygen mild explosions may be produced. This catalytic oxidation is the basis of the large scale manufacture of nitric acid (*see* p. 660).

When ammonia is passed over a heated easily reducible oxide, such as copper oxide, the following reaction occurs—

$$3CuO + 2NH_3 = 3Cu + 3H_2O + N_2 \uparrow$$

Nitrogen is also obtained when excess of ammonia reacts with chlorine,

$$3Cl_2 + 2NH_3 = 6HCl + N_2 \uparrow$$

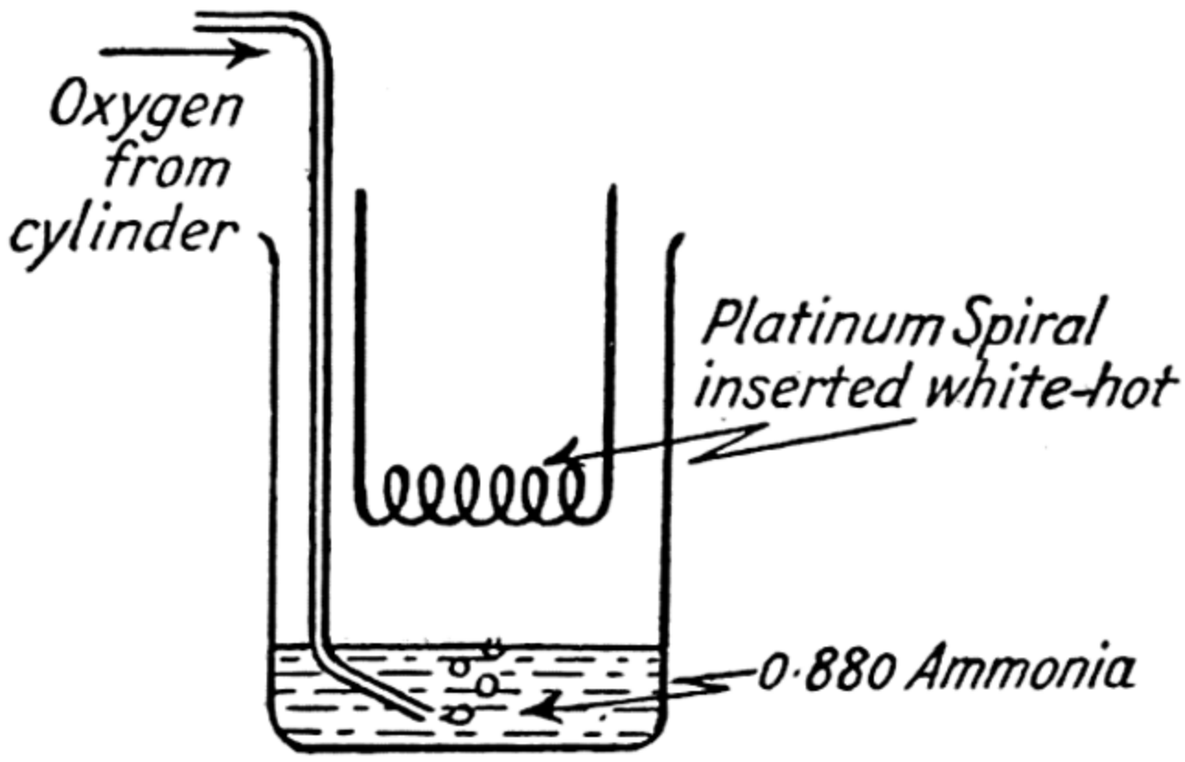


FIG. 205. Catalytic Oxidation of Ammonia

but if the chlorine is in excess, the explosive oil, nitrogen trichloride, is formed—

$$3Cl_2 + NH_3 = NCl_3 + 3HCl \uparrow$$

In the case of iodine, the complex $NH_3 . NI_3$, an insoluble brownish-black compound, known as *nitrogen tri-iodide*, is formed. It is thought that similar addition compounds are formed initially in the corresponding reactions with chlorine and ammonia, but are too unstable to be isolated. With ammonium *salts*, however, the corresponding reactions are—

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl$$

whereas,
$$NH_4Br + Br_2 \rightarrow NH_4Br_3$$

and
$$NH_4I + I_2 \rightarrow NH_4I_3$$

Ammonia combines directly with some metals on heating under water-free conditions. Thus, dry ammonia over sodium metal heated to about 300°C forms sodamide, $NaNH_2$. Magnesium however forms the nitride—

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$
$$3Mg + 2NH_3 = Mg_3N_2 + 3H_2$$

Both sodamide and magnesium nitride are immediately decomposed by water to reliberate ammonia gas.

Large quantities of urea are now produced from ammonia by reaction with carbon dioxide. The ammonia and carbon dioxide are reacted together at about 190°C under 100 atmospheres pressure to form first ammonium carbamate which then decomposes to form urea—

$$CO_2 + 2NH_3 = NH_4 . CONH_2 \rightarrow \underset{\text{urea}}{(NH_2)_2CO} + H_2O$$

Urea is used extensively in the manufacture of urea-formaldehyde resins and plastics, and also finds application as a very rich nitrogenous fertilizer.

Formula of Ammonia. This may be determined by Hofmann's method, based on the reaction—

$$2NH_3 + 3Cl_2 = N_2 + 6HCl$$

A long hard-glass tube, as shown in the diagram, is filled with chlorine gas and strong ammonia solution placed in the cup. After cooling the tube, followed by opening the tap slightly, ammonia enters drop by drop, and white fumes of ammonium chloride form. After adding sufficient ammonia, the tap is closed, and the tube inverted in a cylinder of water. The tap is again opened so that water is drawn into the tube. It will be found on equalizing the pressure to atmospheric, and allowing the temperature to return to its initial value, that the residual insoluble gas occupies one-third the volume of the tube. This gas is nitrogen.

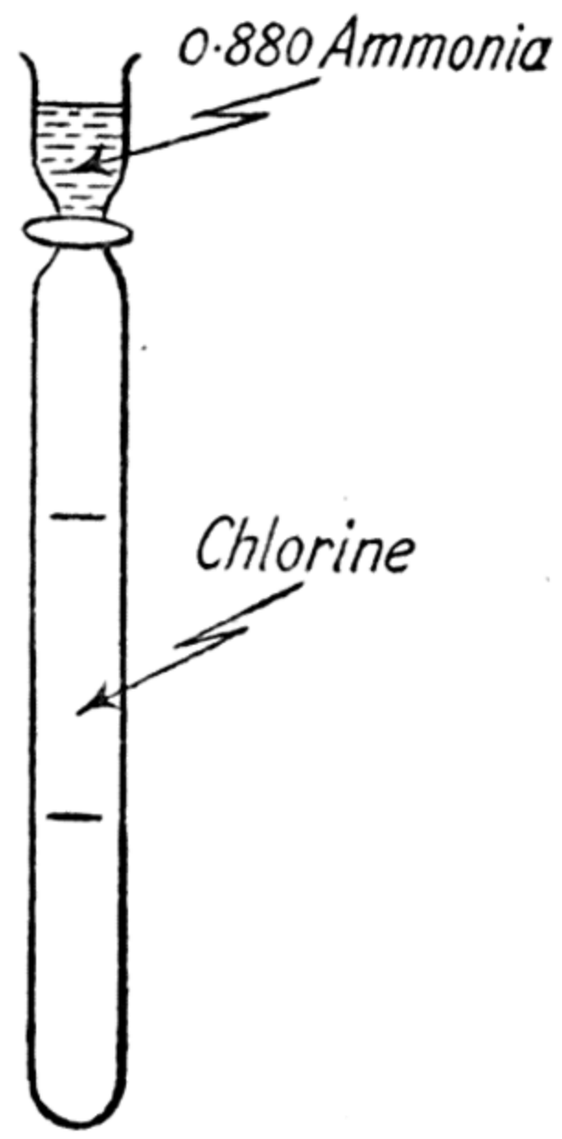


FIG. 206.
Hofmann's Apparatus for Demonstrating the Formula of Ammonia

Thus,

3 volumes of Cl_2 + ammonia → 1 volume of N_2

The chlorine is removed as the very soluble hydrogen chloride (HCl), to form which one volume of chlorine requires one volume of hydrogen, since—

$$H_2 + Cl_2 = 2HCl$$

The three volumes of chlorine therefore obtain three volumes of hydrogen from the ammonia, so liberating one volume of nitrogen.

$$\text{Ammonia} \rightarrow 3 \text{ volumes } H_2 + 1 \text{ volume } N_2$$

Applying Avogadro's hypothesis, it follows that the formula of ammonia is either NH_3, or some simple multiple, such as N_2H_6, etc. We say that the *empirical formula* of ammonia is NH_3. To find the molecular formula, it is necessary to know the molecular weight, and this is obtained

from the vapour density 8·5. The molecular weight of 17 corresponds with the molecular formula NH_3.

Alternatively, a measured volume of ammonia gas is confined over mercury in a eudiometer-tube. On passing electric sparks, the ammonia decomposes into nitrogen and hydrogen. The volume of hydrogen so produced is determined by adding excess oxygen and sparking to form water (the volume of hydrogen being two-thirds of the contraction which occurs at this stage), the volume of nitrogen being found subsequently by absorbing the excess oxygen with alkaline pyrogallol. It is found that two volumes of ammonia gas produce three volumes of hydrogen and one volume of nitrogen, whence, by Avogadro's hypothesis—

$$2N_xH_y = 3H_2 + N_2$$

The molecular formula of ammonia is therefore NH_3.

Detection of Ammonia. The gas is readily detected by its characteristic smell. Less distinctive is its alkaline reaction to litmus. Ammonium salts are similarly recognized by the evolution of ammonia on boiling the salt with aqueous sodium hydroxide.

In the routine analysis of domestic water supplies, it is necessary to test for extremely small quantities of both free and combined ammonia. If a positive test is obtained, it indicates that the water must at some stage have come into contact with decaying animal matter. The test is carried out colorimetrically, using Nessler's solution. The latter may be prepared by adding a slight excess of a solution of potassium iodide to one of mercuric chloride. The red precipitate of mercuric iodide, which is first formed, dissolves in the excess potassium iodide to give a water-clear solution of the complex salt, potassium mercuri-iodide, $K_2[HgI_4]$. This solution is made alkaline with sodium hydroxide to give Nessler's solution.

$$2KI + HgCl_2 = 2KCl + HgI_2\downarrow$$
$$2KI + HgI_2 = K_2[HgI_4]$$

In presence of free and of combined ammonia, Nessler's solution turns yellow, or brown, depending upon the ammonia concentration.

Uses of Ammonia. The liquid or solution is used in refrigerators, and in the large-scale manufacture of (*a*) fertilizers, such as ammonium sulphate, ammonium nitrate and ammonium phosphate, (*b*) nitric acid and nitrates, (*c*) urea, and (*d*) certain other organic compounds such as aniline.

It is used in the nitriding of steel to produce a very hard surface layer, and also with chlorine, in the sterilization of water supplies. Considerable quantities are also used as a convenient source of hydrogen and nitrogen, which are produced by the thermal decomposition of the ammonia in suitable apparatus. In this way a relatively inert mixture of nitrogen and hydrogen suitable as a furnace atmosphere in the heat treatment of metals and alloys may be obtained.

Ammonium Hydroxide and Ammonium Salts

The solution of ammonia in water contains a weak alkali, known as ammonium hydroxide—

$$NH_3 + H_2O \rightleftharpoons \underset{\text{ammonium hydroxide}}{NH_4OH} \rightleftharpoons NH_4^+ + OH^-$$

When neutralized with an acid, the corresponding ammonium salts are formed. Thus hydrochloric acid gives ammonium chloride—

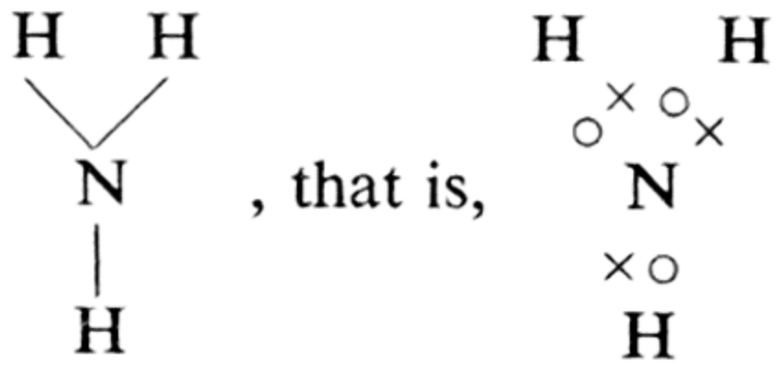
$$NH_4OH + HCl = NH_4Cl + H_2O$$

The ammonium salts all contain the ammonium ion, NH_4^+, which is to be regarded as a univalent ion, just as is the sodium ion, Na^+, etc. Unlike the latter, however, the ammonium ion cannot exist alone in the uncharged state; that is, ammonium, NH_4, does not exist. The student must therefore distinguish between—

(*a*) the molecule NH_3, which exists as a definite compound, ammonia; and

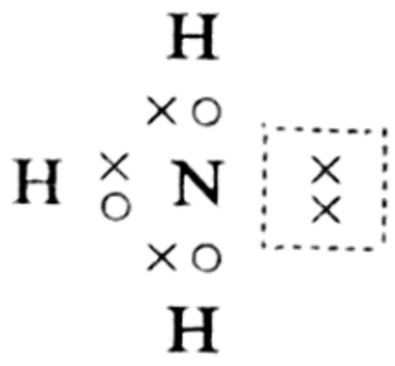
(*b*) the ammonium ion, NH_4^+, which occurs only in the form of salts or the hydroxide.

The difference between ammonia and ammonium is briefly that ammonia is a gas having the covalent structure



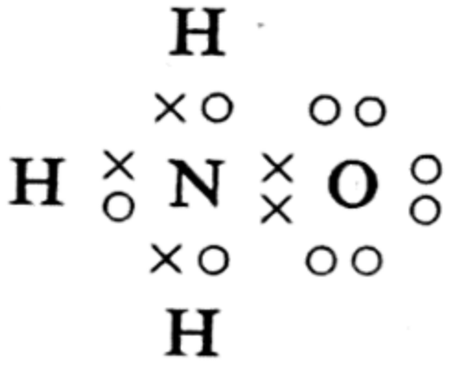
In the absence of moisture it is neither acidic nor basic. The ammonium ion, on the other hand, is positively charged and cannot exist alone, resembling in this respect the sulphate ion, SO_4^{--}, the nitrate ion, NO_3^-, etc.

The changes involved in the conversion of ammonia into the ammonium ion result from the presence of a "lone pair" of electrons (shown within the dotted line) on the nitrogen atom,



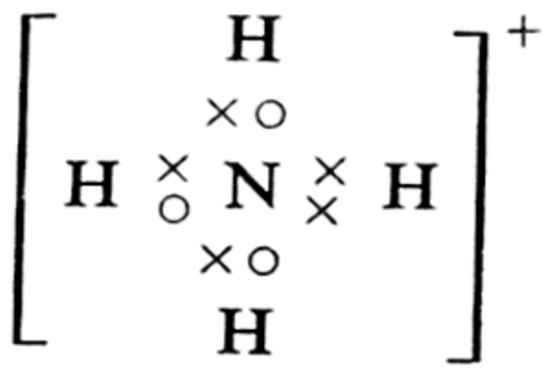
It will be observed that in the electronic structure of ammonia, the central

nitrogen atom has acquired its full complement or octet of electrons. It is possible however, for the nitrogen to attach another atom by means of its "lone pair" of electrons, thus



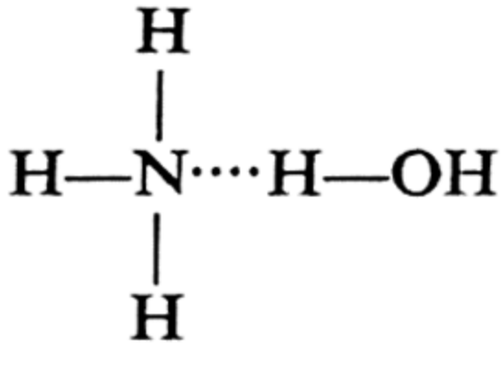
Although this particular compound does not exist, its organic counterpart tri-methylamine oxide does, $(CH_3)_3N \rightarrow O$ (*see* p. 950).

The ammonium ion may similarly be regarded as the product of the addition of a hydrogen ion to ammonia $NH_3 + H^+ \rightarrow (NH_4)^+$, the latter having the electronic structure



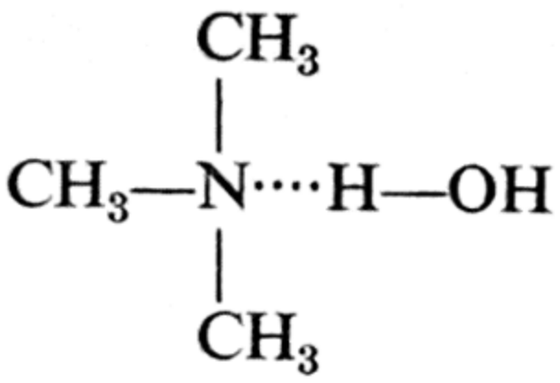
The electrons depicted as "×" and "○" are of course identical, so that the four hydrogen atoms are indistinguishable from one another and the positive charge is regarded as associated with the ion as a whole.

The fact that ammonium hydroxide is a weak alkali implies that appreciable association of the NH_4^+ and OH^- ions occurs to form the un-ionized covalent ammonium hydroxide, the structure of which is presumably

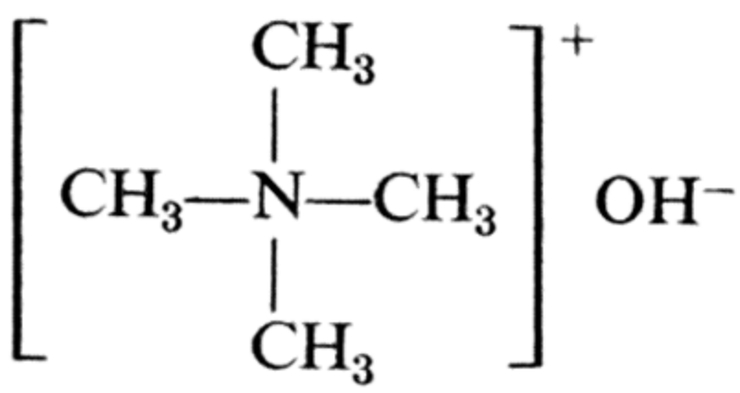


involving the formation of a *hydrogen bond* between the nitrogen and hydroxyl groups. If, however, the hydrogen atoms of the ammonium ion are progressively replaced by alkyl groups such as CH_3 the resulting compounds become increasingly more basic and it is noteworthy that when all the hydrogen atoms have been replaced in this way, to form for example tetra-methyl ammonium hydroxide, a very considerable increase in the alkalinity occurs. This presumably results from the remote possibility of a hydrogen bond between the hydrogen atom of a methyl group and the hydroxyl group, so that the compound is in fact

completely ionized and is a strong alkali, like sodium hydroxide. Compare—



(moderately strong base)



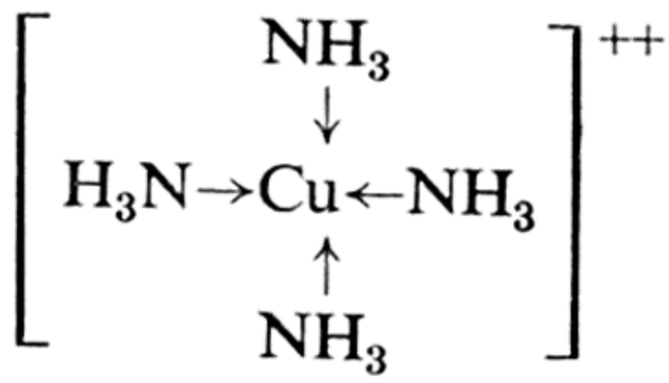
(very stong base)

Like the alkalis, ammonium hydroxide will precipitate insoluble hydroxides, such as ferrous hydroxide, etc., but in the case of copper salts the precipitate of cupric hydroxide which is first formed dissolves in excess of the ammonium hydroxide to form a deep-blue solution of cuprammonium hydroxide—

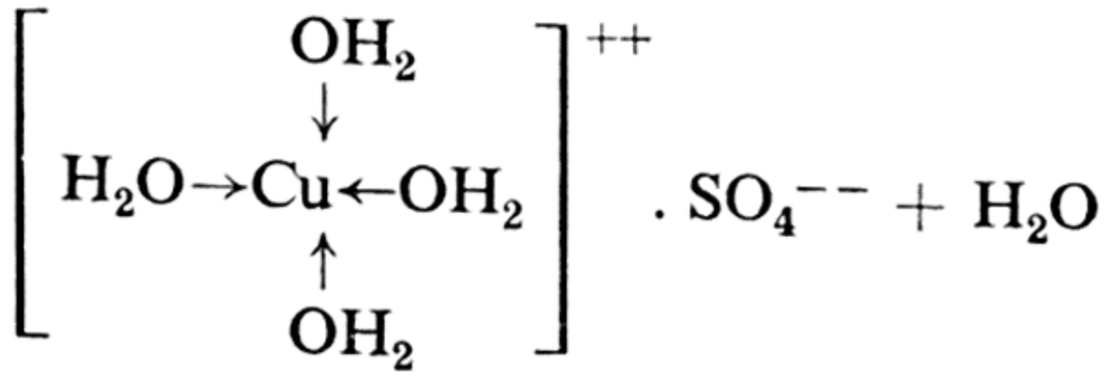
$$Cu(OH)_2 + 4NH_4OH = [Cu(NH_3)_4](OH)_2 + 4H_2O$$

Solutions of cuprammonium hydroxide will dissolve cellulose (filter-paper, cotton wool, etc.) to form a viscous solution which reprecipitates the cellulose when it is acidified. This sequence of reactions was formerly used in the manufacture of artificial silk, and may be demonstrated in the laboratory by forcing such a solution from a small jet into a trough of sulphuric acid to neutralize the ammonia. The cellulose is reprecipitated in the form of a long continuous thread.

The structure of the ammines of which the cuprammonium salts are but one example of many, involve the linkage of the ammonia molecule directly to the central metallic atom, the lone pair of electrons of the nitrogen forming a co-ordinate linkage,



Since copper is able to co-ordinate four molecules of ammonia in this way, it is said to have a Co-ordination Number of four. The hydrates of copper salts are similar, and $CuSO_4 . 5H_2O$ is now known to have the structure—



in which the fifth water molecule is not co-ordinated to the copper ion but occupies a spacial position between the tetra-hydrated copper ions and the sulphate ions in the solid structure.

Other examples of ammines include the well known cobalt-ammines and platinum ammines, etc.

The close similarity in structure between the ammines and the crystalline hydrates is due to the fact that both ammonia and water molecules possess a lone pair of electrons and so can add on in the molecular form by means of co-ordinate linkages. Analagous to the hydrates of calcium chloride are the solid ammines such as $CaCl_2 . 8NH_3$, formed when ammonia is passed over calcium chloride. For this reason calcium chloride cannot be used to dry ammonia gas.

Ammonium Salts. These are all soluble, with the exception of the perchlorate, chloroplatinate and cobaltinitrite, and decompose or volatilize on heating. When heated with alkalis, ammonia is liberated. The salts show a closer resemblance in solubility, etc., to the corresponding potassium salts than to the sodium salts, and this is due to the greater similarity in their ionic radii, thus—

$$NH_4^+ = 1{\cdot}43\ \text{Å}, \quad K^+ = 1{\cdot}33\ \text{Å}, \quad Na^+ = 0{\cdot}98\ \text{Å}$$

Ammonium Chloride, NH_4Cl. This is obtained as a white solid on evaporating the solution obtained by neutralizing ammonia with hydrochloric acid. It is purified by sublimation; the ammonium chloride dissociates into the gases ammonia and hydrogen chloride which subsequently recombine at lower temperatures to reform pure ammonium chloride.

$$NH_4Cl \xrightarrow{\text{heat}} NH_3 + HCl \xrightarrow{\text{cool}} NH_4Cl$$

Note, that the term "dissociation" implies that the change is reversible; when it is irreversible, it is called "decomposition"—for example, the decomposition of ammonium nitrite on heating.

Ammonium Sulphate is an important fertilizer, the manufacture of which has already been described on p. 638.

Ammonium Nitrate, NH_4NO_3, is a very valuable nitrogenous fertilizer. In times of war its explosive properties are recognized, and it is used in the Amatols as a diluent of T.N.T. The discovery that ammonium nitrate could safely be mixed with T.N.T. to produce an explosive almost as powerful as 100 per cent T.N.T. was made during the First World War at a time when T.N.T. supplies were becoming short. The Baratols, similarly, consist of mixtures of T.N.T. and barium nitrate. Ammonium nitrate exists in five polymorphic forms, and is thus a good example of polymorphism. The various forms and corresponding transition temperatures are—

$$\text{Tetragonal} \underset{}{\overset{-17^\circ C}{\rightleftharpoons}} \text{Rhombic I} \overset{32{\cdot}1^\circ C}{\rightleftharpoons} \text{Rhombic II} \overset{84{\cdot}2^\circ C}{\rightleftharpoons}$$

$$\text{Rhombohedral} \overset{125{\cdot}2^\circ C}{\rightleftharpoons} \text{Cubic}$$

Hydrazine, N_2H_4 (or, $H_2N—NH_2$). When a strong solution of ammonia is boiled with a freshly made sodium hypochlorite solution in the presence of a little glue, the following reactions occur—

$$NH_3 + NaOCl = NH_2Cl + NaOH$$

$$NH_3 + NH_2Cl = NH_2 . NH_2 + HCl \uparrow$$

The glue helps to prevent any appreciable formation of compounds such as $NHCl_2$ and NCl_3. If the solution is cooled and acidified with dilute sulphuric acid, colourless crystals of hydrazine sulphate, $N_2H_4 . H_2SO_4$, are obtained.

If hydrazine sulphate is distilled under reduced pressure with a strong alkali, a colourless fuming liquid, known as *hydrazine hydrate*, $N_2H_4 . H_2O$, is obtained. Reducing the pressure lowers the boiling point, and the practice of distilling under reduced pressure is usual when the compound tends to decompose at its normal boiling point under atmospheric pressure. Hydrazine hydrate boils with decomposition at 119°C, but under 26 mm pressure for example it boils at 47°C without much decomposition.

Anhydrous hydrazine may be prepared by distilling the mono-hydrate with barium oxide—

$$N_2H_4 . H_2O + BaO = Ba(OH)_2 + N_2H_4$$

Hydrazine is a very weak diacidic base and forms two series of salts, $N_2H_4 . HCl$ and $N_2H_4 . 2HCl$; $(N_2H_4)_2 . H_2SO_4$ and $N_2H_4 . H_2SO_4$. Both hydrazine and its salts are very powerful reducing agents. They precipitate gold, silver and platinum from solutions of their salts, cuprous oxide from alkaline cupric solutions, and reduce ferric iron solutions, iodates and free iodine. The latter reaction may be used to estimate hydrazine in solution—

$$N_2H_4 + 2I_2 = N_2 + 4HI$$

Hydrazoic Acid, HN_3. When dry ammonia is passed over heated sodium, the compound sodamide is formed. If the latter is heated at 190°C in a current of nitrous oxide, sodium azide is obtained—

$$NaNH_2 + N_2O = NaN_3 + H_2O$$

Hydrazoic acid, a colourless liquid, boiling point 37°C, may be prepared by distilling sodium azide with dilute sulphuric acid—

$$NaN_3 + H_2SO_4 = NaHSO_4 + HN_3$$

It has an unpleasant smell and is very explosive and poisonous.

The solution behaves like a typical acid, liberating hydrogen with metals such as iron and zinc and forms salts, known as azides. The azides

appear to fall into two categories, (*a*) dangerously explosive and (*b*) moderately stable. The former include the azides of the heavy metals, such as lead azide, $Pb(N_3)_2$ and are thought to have the non-ionized covalent structure based on the resonance forms (*see* p. 73) of the un-ionized hydrazoic acid—

$$H—N=N\rightarrow N \quad \rightleftharpoons \quad H—N\leftarrow N\equiv N$$

So sensitive are these azides, that extremely small quantities are used to initiate on percussion the detonation of bulk explosives such as C.E. and T.N.T. in bombs, etc. The second class include the azides of the alkalis and alkaline-earth metals. These are ionic, the azide ion being a resonance hybrid of the two structures—

$$[N\equiv N\rightarrow N]^- \quad \rightleftharpoons \quad [N=N\rightarrow N]^-$$

Hydroxylamine, NH_2OH. Hydroxylamine may be prepared by the reduction of nitric acid either electrolytically using a pure mercury or amalgamated metal cathode, or by the action of tin and hydrochloric acid. In the latter method, stannous chloride is formed and precipitated as stannous sulphide by diluting the solution and passing in sulphuretted hydrogen. The solution is then concentrated by evaporation to give hydroxylamine hydrochloride, NH_2OH . HCl. The latter, when distilled under reduced pressure with sodium methoxide in methyl alcohol solution, produces anhydrous hydroxylamine. This is a colourless solid, melting at 33°C, and easily decomposed to liberate ammonia and nitrogen—

$$3NH_2OH = NH_3\uparrow + N_2\uparrow + 3H_2O$$

Hydroxylamine is a weak base and forms salts such as hydroxylamine hydrochloride, $(NH_3OH)Cl$, analogous in formula to ammonium chloride, NH_4Cl. Both the base and its salts are powerful reducing agents, precipitating cuprous oxide from alkaline cupric solutions, metallic gold from auric chloride, $AuCl_3$ solution, and reducing ferric iron solutions.

Both hydroxylamine and hydrazine condense with the organic compounds known as aldehydes and ketones, which contain the carbonyl group—

$$\rangle C=\boxed{O + H_2}N—OH \rightarrow \rangle C=N—OH + H_2O$$

$$\rangle C=\boxed{O + H_2}N—NH_2 \rightarrow \rangle C=N—NH_2 + H_2O$$

to form compounds known respectively as oximes and hydrazones. These are solid crystalline compounds and are often prepared in order to identify or purify the parent aldehyde or ketone (*see* p. 910).

Oxides and Oxy-acids of Nitrogen

Oxides	*Acids*
Nitrous oxide, N_2O	Hyponitrous acid, $H_2N_2O_2$
Nitric oxide, NO	
Nitrous anhydride, N_2O_3	Nitrous acid, HNO_2
Nitrogen peroxide, NO_2, N_2O_4	
Nitric anhydride, N_2O_5	Nitric acid, HNO_3
Nitrogen trioxide, NO_3	

The oxides are all endothermic compounds, that is, they are formed from nitrogen and oxygen with an absorption of heat. When they are

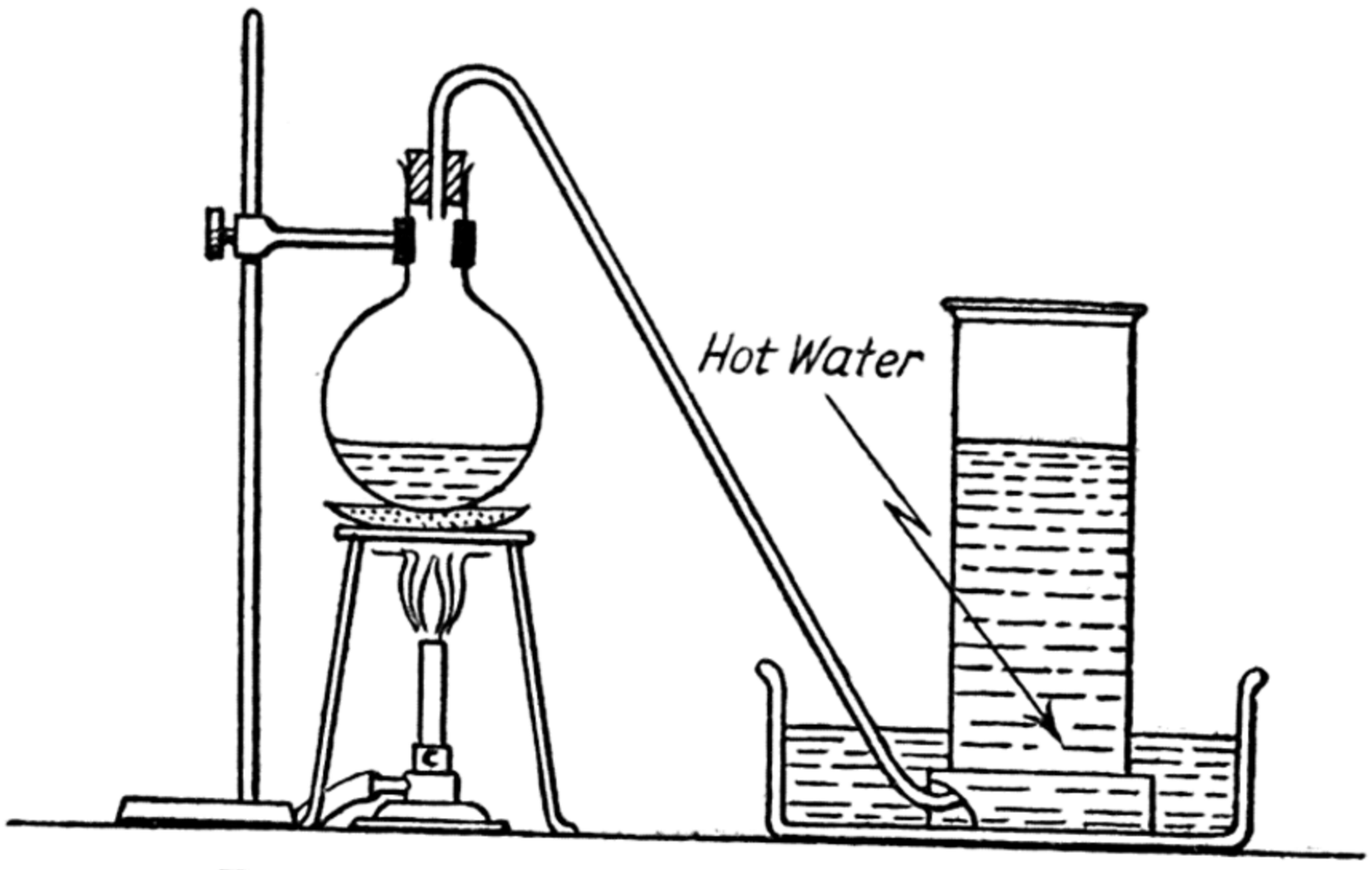


FIG. 207. Preparation of Nitrous Oxide

decomposed, therefore, they liberate heat, and this promotes further decomposition. They may be arranged in approximate order of increasing stability as follows—

$$\{N_2O_3, NO_3, N_2O_5\} < N_2O < NO_2 < NO$$

They are also decomposed to liberate nitrogen when passed over strongly heated copper or iron, etc.

$$Cu + N_2O = CuO + N_2 \uparrow$$

and such a reaction may be used in establishing their respective molecular formulae.

Nitrous Oxide, N_2O, may be prepared by cautiously heating ammonium nitrate (or ammonium chloride and sodium nitrate mixture) and collecting the gas over hot water—

$$NH_4NO_3 = N_2O \uparrow + 2H_2O \uparrow$$

The nitrate first melts, and then begins to decompose as above. The reaction is exothermic and may proceed explosively if heated too strongly. The gas may be purified, from nitric oxide via a solution of ferrous sulphate, from chlorine (introduced by ammonium chloride impurity) and acid gases via strong sodium hydroxide solution and, after drying by bubbling through concentrated sulphuric acid, may be collected over mercury.

Pure nitrous oxide may be prepared directly by the irreversible decomposition of hyponitrous acid on heating—

$$H_2N_2O_2 \rightarrow H_2O + N_2O$$

The hyponitrous acid is prepared in situ by mixing equimolecular quantities of sodium nitrite and hydroxylamine hydrochloride—

$$HO—N\boxed{H_2 + O}=N—OH \rightarrow \boxed{H-}\boxed{-O—N=N-}\boxed{-OH}$$

$$(N_2O + H_2O)$$

Properties of Nitrous Oxide. A colourless gas with a sweetish odour, it may be liquefied at $-90°C$, and is appreciably soluble in water (1:1 at about 6°C). The solution in water is neutral, so that the reaction whereby it is produced by the decomposition of hyponitrous acid is not reversible, and nitrous oxide is not the true anhydride of this acid.

Nitrous oxide was one of the earliest anaesthetics to be used, and is still used, particularly in dental surgery.

The chemical behaviour of the gas appears to be related to the ease with which it dissociates into nitrogen and oxygen on heating—

$$2N_2O \rightleftharpoons 2N_2 + O_2 + 41\,000 \text{ cal.}$$

Thus, like oxygen, it will relight a glowing splint, and support the combustion of burning magnesium, sodium, phosphorus, sulphur, carbon, etc. It may be distinguished from oxygen however by such differences as—

(*a*) Oxygen is absorbed by alkaline pyrogallol (the latter turning deep brown); nitrous oxide is not absorbed.

(*b*) Oxygen gives brown fumes when mixed with nitric oxide; nitrous oxide does not.

(*c*) No change in volume occurs when phosphorus is allowed to burn in nitrous oxide; but when phosphorus burns in oxygen the volume decreases continuously during the reaction.

$$5N_2O + 2P = P_2O_5 + 5N_2$$

(*d*) Nitrous oxide has a faint smell and is heavier than oxygen (22, cf. 16).

Formula of Nitrous Oxide. The formation of nitrogen and oxygen when nitrous oxide is heated shows that only these two elements are present. The vapour density of 22 gives the molecular weight as 44 and hence the

molecular formula N_2O. Since, however, the molecular weight of 44 is so close to that for the molecule NO_2, namely 46, the formula derived above may be confirmed by heating an iron wire or copper turnings in the gas. It is observed that—

1 volume of nitrous oxide → 1 volume of nitrogen

Therefore, by Avogadro's hypothesis, $N_xO_y \rightarrow N_2$, and the formula is N_2O_y. The molecular weight of 44 now indicates y to be 1, and the true molecular formula to be N_2O.

Structure. Nitrous oxide appears to be a resonance hybrid of—

$$N\rightleftarrows N=O \text{ and } N\equiv N\rightarrow O$$

Nitric Oxide, NO. Nitric oxide is readily prepared by the action of nitric acid diluted with an equal volume of water on copper turnings.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$

It may be collected over water in the usual way, or may be purified by absorbing it in a strong solution of ferrous sulphate, when a brown nitroso-complex, $FeSO_4 . NO$, forms, and the other gases pass on. The nitric oxide is then reliberated on heating this solution.

Pure nitric oxide may be prepared by the same sequence of reactions as occur in the "brown-ring" test for nitrates. A solution of ferrous sulphate and a nitrate is treated with concentrated sulphuric acid and mixed. The ferrous sulphate is oxidized by the nitric acid formed from the nitrate, and nitric oxide is liberated. The solution turns brown due to the formation of the $FeSO_4 . NO$ complex, but the heat of the reaction is sufficient to decompose this and liberate free nitric oxide—

$$2FeSO_4 + H_2SO_4 + \overline{O} = Fe_2(SO_4)_3 + H_2O \quad . \quad . \quad \text{(i)}$$

$$2HNO_3 = 2NO + H_2O + 3\overline{O} \quad . \quad . \quad \text{(ii)}$$

From these two basic equations is obtained the following equation for the reaction—

$$6FeSO_4 + 3H_2SO_4 + 2NHO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO\uparrow$$

In the presence of mercury and concentrated sulphuric acid, nitrates and nitrites are converted quantitatively into nitric oxide, the volume of gas so produced being a measure of the original nitrate or nitrite concentration—

$$6Hg + 2HNO_3 + 3H_2SO_4 = 3Hg_2SO_4 + 2NO\uparrow + 4H_2O$$

$$2Hg + 2HNO_2 + H_2SO_4 = Hg_2SO_4 + 2NO\uparrow + 2H_2O$$

Properties of Nitric Oxide. It is a colourless gas, and may be liquefied at $-150°C$ and solidified at $-160°C$. It is slightly soluble in water, but is

very soluble in solutions of ferrous salts with which it forms brown nitroso-complexes such as $FeSO_4 . NO$.

Nitric oxide also combines directly with oxygen, for example, when exposed to the air, to form the brown gas, nitrogen peroxide—

$$2NO + O_2 = 2NO_2$$

Its odour is consequently unknown. This latter reaction was put to commercial account in the manufacture of nitric acid by the Arc Process; it also occurs in the fixation of atmospheric nitrogen during electrical storms, the sequence of reactions being—

(*a*) $$N_2 + O_2 = 2NO$$

(*b*) $$2NO + O_2 = 2NO_2$$

(*c*) $$3NO_2 + H_2O = 2HNO_3 + NO$$

The reaction (*a*) is both reversible and endothermic, and the equilibrium yield of nitric oxide increases with temperature, increasing from less than a half of one per cent at 1000°C to about 5 per cent at 3000°C. Both the forward and reverse reactions occur increasingly slowly with reduction in temperature, being very slow about 1000°C. Below this temperature, therefore, nitric oxide is relatively stable, and very little decomposition into nitrogen and oxygen occurs. For this reason, nitric oxide does not support the combustion of burning sulphur or of glowing charcoal, although it will support that of magnesium, phosphorus and sodium, owing to the higher temperatures produced. Nitric oxide is in fact the most stable of the oxides of nitrogen.

When a gas-jar of nitric oxide is shaken with a little carbon disulphide, and a light applied, a brilliant blue flash is produced and a deposit of sulphur formed on the sides of the jar. The flash is very rich in ultra-violet radiation, and was formerly used as a flash-light for photographic purposes. The experiment should not be carried out too frequently as ultra-violet radiation damages the eyes. The precise nature of the reactions involved are obscure.

Nitric oxide combines directly with chlorine in presence of charcoal to form nitrosyl chloride, NOCl—

$$2NO + Cl_2 = 2NOCl$$

The addition reaction of nitric oxide with solutions of ferrous salts to form complex nitrosyl compounds also occurs with the carbonyl compounds of iron and cobalt to form volatile red liquids, such as $Fe(CO)_2(NO)_2$ and $Co(CO)_3(NO)$, known as *nitrosyl carbonyls*. Nitric oxide is also absorbed by alkaline solutions of sulphites to form, in the case of potassium sulphite, the compound $K_2SO_3 . 2NO$. With acids the latter is decomposed to liberate nitrous oxide quantitatively—

$$K_2SO_3 . 2NO = K_2SO_4 + N_2O \uparrow$$

and when reduced, for example by means of sodium amalgam and water, produces small quantities of hydrazine, N_2H_4.

Formula of Nitric Oxide. The fact that nitric oxide combines immediately with oxygen at ordinary temperatures makes the determination of its vapour density one of some difficulty. This difficulty may be avoided by determining the molecular formula as follows.

(*a*) A measured volume of the gas is decomposed by an electrically heated iron wire, and the volume of nitrogen measured.

Two volumes of nitric oxide → one volume of nitrogen

whence, by Avogadro's hypothesis—

$$2N_xO_y \rightarrow N_2$$

Thus, $x = 1$, and the formula is NO_y

(*b*) A measured volume of the gas is decomposed into nitrogen and carbon dioxide on strongly heating charcoal in the gas, and the volume of carbon dioxide determined by measuring the change in volume on adding a little strong alkali.

Two volumes of nitric oxide → one volume of carbon dioxide

whence, by Avogadro's hypothesis—

$$2NO_y \rightarrow CO_2$$

Thus, $y = 1$, and the molecular formula is NO.

Electronic Structure. Nitric Oxide appears to be a resonance hybrid of the two structures—

(*a*) N=O and (*b*) N⇇O

For a full discussion of the structure of the oxides of nitrogen *see* p. 656.

Nitrous Anhydride, N_2O_3. In the vapour phase, the gas is almost completely dissociated into nitric oxide and nitrogen peroxide—

$$N_2O_3 = NO + NO_2$$

It exists however in the liquid phase and probably also in the solid phase, and is blue in colour.

If arsenious oxide is distilled with 60 per cent nitric acid and the gases condensed in a freezing mixture in the absence of air, the pale blue liquid N_2O_3 is obtained—

$$As_2O_3 + 2HNO_3 = As_2O_5 + NO\uparrow + NO_2\uparrow + H_2O$$
$$NO + NO_2 = N_2O_3$$

If a solution of a nitrite is acidified in the cold, a pale blue solution is

obtained. The colour is due to the formation of free N_2O_3 by decomposition of the nitrous acid—

$$NaNO_3 + HCl = NaCl + HNO_2\ (+ O)$$
$$2HNO_2 = H_2O + N_2O_3$$

Nitrogen Peroxide, NO_2 and N_2O_4. The usual laboratory method of preparation is to heat lead nitrate crystals in a hard-glass tube and condense the nitrogen peroxide in a U-tube immersed in a freezing mixture of ice and water.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2\uparrow + O_2\uparrow$$

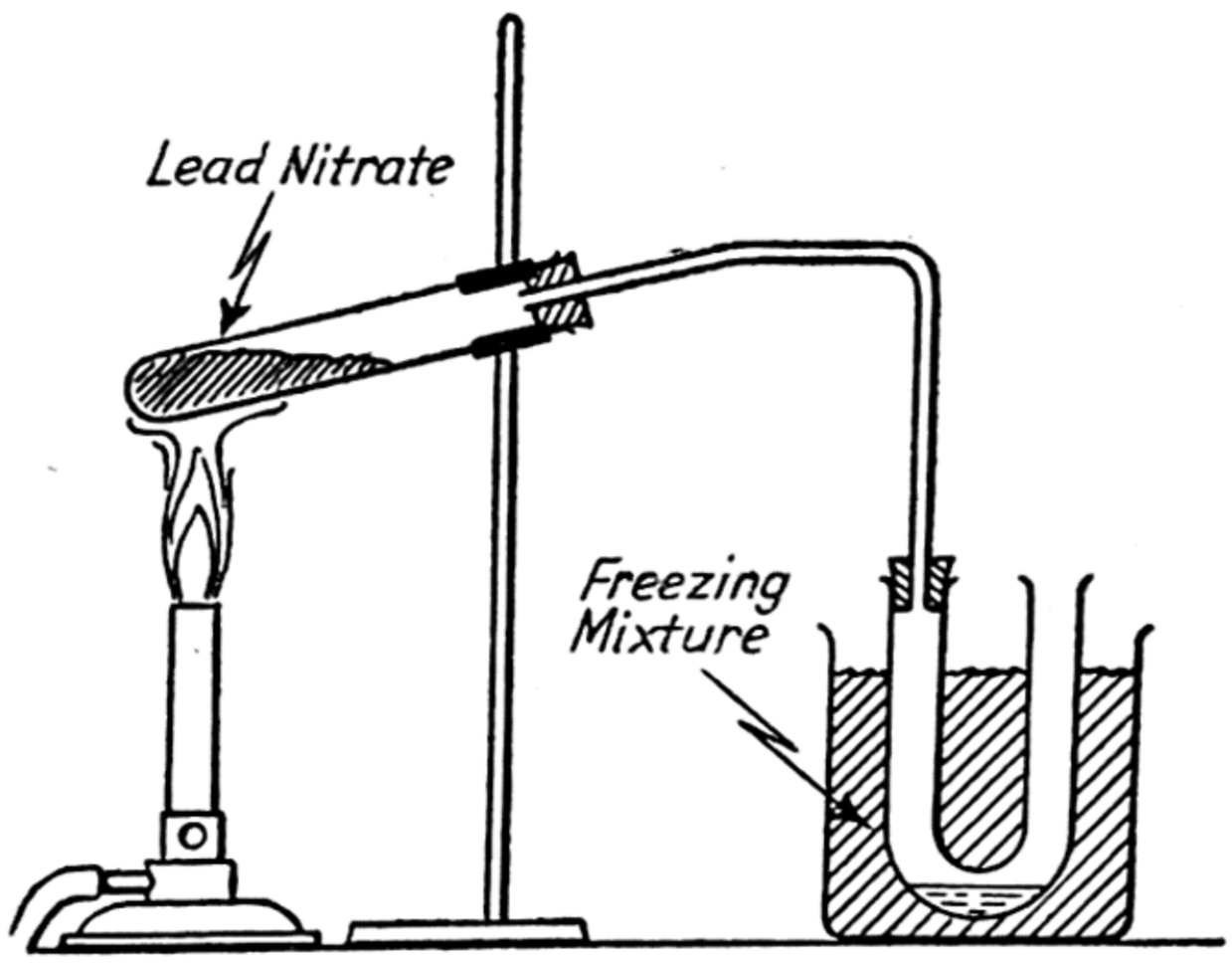


FIG. 208. Preparation of Nitrogen Peroxide

Nitrogen peroxide is also obtained as a result of the action of concentrated nitric acid on copper turnings—

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

Nitrogen peroxide is also formed by the direct combination of nitric oxide and oxygen at ordinary temperatures.

Properties of Nitrogen Peroxide. Nitrogen peroxide may be liquefied at 22°C and solidified at − 10°C. The solid is colourless when pure, and the liquid a pale yellow colour. The depth of colour increases progressively as the temperature is increased from the melting point up to about 150°C when the gas is deep brown in colour. With further increase in temperature the depth of colour decreases, and it is completely colourless at about 620°C. These colour changes result from the following dissociation reactions, and occur in reverse on cooling—

$$N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$$

The solid consists of the colourless "double" molecules N_2O_4. These dissociate on heating to form the brown NO_2 molecules, the dissociation

being complete at 150°C. Above this temperature, the NO_2 dissociates into the colourless oxygen and nitric oxide, the dissociation in this case being complete at the higher temperature of 620°C.

The proportion of NO_2 molecules present at any temperature up to 150°C is usually determined from the vapour density of the gas. Considering the equilibrium—

$$\underset{(1-x)}{N_2O_4} = \underset{2x}{2NO_2}$$

then, if x is the degree of dissociation of the N_2O_4 molecules, the relative increase in the number of molecules present due to the dissociation is given by—

$$\frac{\text{Total number of molecules present}}{\text{Number of } N_2O_4 \text{ molecules (if no dissociation occurs)}} = (1 + x)$$

By Avogadro's hypothesis, therefore—

$$\frac{\text{Final volume with dissociation } x}{\text{Volume if no dissociation occurred}} = (1 + x)$$

and, since the volumes for a given weight of nitrogen peroxide are inversely proportional to the densities, it follows that—

$$\frac{\text{Vapour density of } N_2O_4}{\text{Actual vapour density}} = \frac{46}{d} = (1 + x)$$

Knowing d, the vapour density of the nitrogen peroxide, the degree of dissociation, x, may then be determined. This value gives directly the proportion of NO_2 by weight in the gas. The proportion by volume will be seen to be—

$$\frac{\text{Volume of } NO_2}{\text{Total volume of } NO_2 \text{ and } N_2O_4} = \frac{\text{Number of molecules of } NO_2}{\text{Number of molecules of } NO_2 \text{ and } N_2O_4}$$

$$= \frac{2x}{(1-x) + 2x} = \frac{2x}{1 + x}$$

Nitrogen peroxide dissolves in water in the cold to form nitric and nitrous acids, and is therefore a mixed anhydride—

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

At ordinary temperatures or higher, the nitrous acid decomposes—

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

and the net equation of the reaction of nitrogen peroxide with water becomes—

$$H_2O + 3NO_2 = 2HNO_3 + NO$$

When nitrogen peroxide is absorbed in aqueous alkalis, the corresponding nitrates and nitrites are formed, thus—

$$2NaOH + 2NO_2 = NaNO_3 + NaNO_2 + H_2O$$

Nitrogen peroxide supports combustion more vigorously than nitric oxide but less so than nitrous oxide. Thus vigorously burning phosphorus, charcoal, sodium and potassium all continue to burn in the gas to liberate free nitrogen.

Sulphur dioxide in presence of water is oxidized to sulphuric acid—

$$H_2SO_3 + NO_2 = H_2SO_4 + NO$$

as described in connexion with the Lead Chamber Process (*see* p. 751).

Formula. The reaction of nitrogen peroxide with strongly heated charcoal to form carbon dioxide and nitrogen enables the empirical formula NO_2 to be determined, following the method outlined in connexion with nitric oxide. Determination of the vapour density then shows the gas to be composed of molecules of NO_2 and of N_2O_4.

Nitric Anhydride, N_2O_5. Crystals of nitric anhydride may be obtained by passing ozonized oxygen through cooled liquid nitrogen peroxide. It may also be prepared by dehydrating fuming nitric acid with phosphorus pentoxide. The crystals are white and very hygroscopic; they decompose slowly at ordinary temperature and more rapidly on warming.

$$2N_2O_5 = 4NO_2\uparrow + O_2\uparrow$$

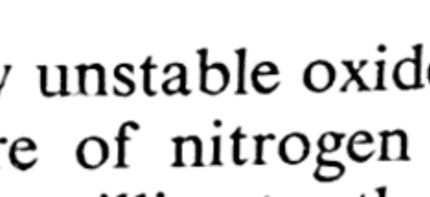
It is a powerful oxidizing agent and attacks rubber and cork. These materials should therefore be absent from any apparatus used to prepare and collect the oxide.

Nitrogen Trioxide, NO_3. This very unstable oxide is reported as having been prepared by passing a mixture of nitrogen peroxide and oxygen (1:20 by volume) at a pressure of one millimetre through a glow discharge in a U-shaped discharge tube. By cooling the lower portion of the discharge tube in liquid air, a white solid was obtained, which decomposed above − 140°C into nitrogen peroxide and oxygen. Other workers claim to have obtained definite evidence of nitrogen trioxide gas by allowing nitrogen dioxide and ozone to vaporize together.

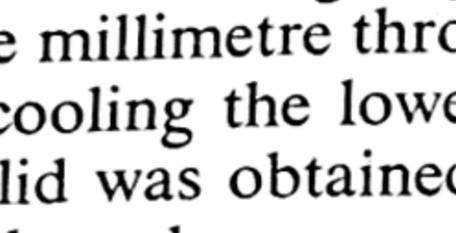
Electronic Structure of the Oxides of Nitrogen

Nitric oxide appears to be a resonance hybrid of the two structures—

(*a*) $\acute{N}{=}O$, that is,



(*b*) $N{\leftarrow}\acute{O}$, that is,

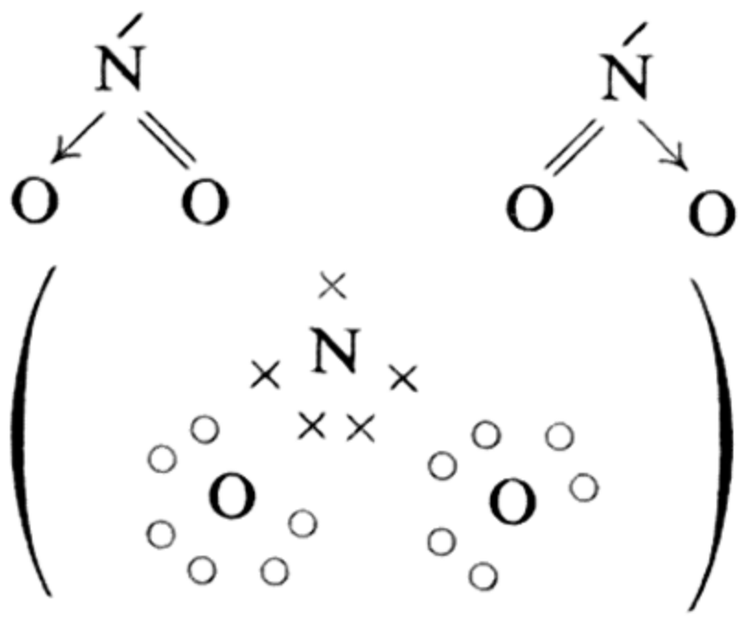


In the first of these, it will be seen that the oxygen has acquired the two electrons necessary to complete its outer octet of electrons but that the nitrogen atom is still one electron short, this deficiency being denoted by the superscript ´. In the second structure, in which a covalent link and a co-ordinate link unite the two atoms, the electron deficiency has passed to the oxygen atom. No other structures appear possible.

On the *resonance theory* (*see also* p. 73) the actual structure is considered to be neither (*a*) nor (*b*), but a resonance hybrid of these. In its normal state, the gas is regarded as having a structure intermediate between (*a*) and (*b*), in which the electron deficiency of the N— atom in (*a*) and of the O— atom in (*b*) are approximately balanced. Such a structure cannot satisfactorily be depicted by a single electronic structure, and it is customary to refer to it as a resonance hybrid of the two. The student should note particularly that the term resonance hybrid does not imply an equilibrium between the two forms (*a*) and (*b*), and that neither of these forms occur in the unactivated state of the gas.

The results of the resonance are three-fold. The odd-electron deficiency, instead of being associated specifically with the N or O atoms, is instead a deficiency of the molecule as a whole, a conclusion which is supported by the fact that nitric oxide is practically non-polar (that is, it does not behave as a small magnet in an electric field). If the structure were actually either (*a*) or (*b*) or even an equilibrium mixture of these, the gas would be polar. The second result is to stabilize the molecule as compared with the structures (*a*) and (*b*). More energy has to be supplied to dissociate the molecule into nitrogen and oxygen than would be the case for either of the non-resonance structures. The third result concerns the distance apart of the N and O atoms in the molecule. This distance has been measured by electron diffraction technique and shown to be intermediate between the theoretical distances for the (*a*) and (*b*) structures.

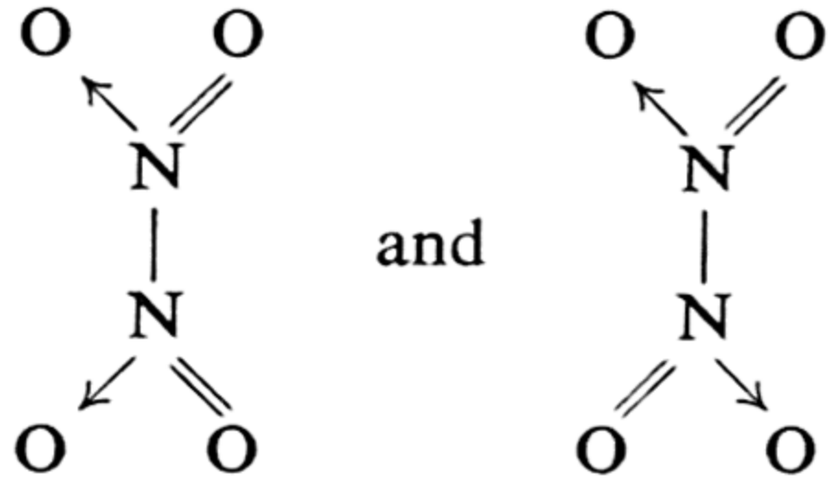
Nitrogen peroxide is also a resonance hybrid, the two forms being—



Examination of these two structures shows that the resonance structure, representing as it does something intermediate between these, must retain on the N— atom a definite deficiency of one electron. This deficiency, specifically associated with the nitrogen atom, probably accounts for—

(i) The non-linear shape of the molecule,

(ii) the deep-brown colour of the gas, and
(iii) the tendency to polymerize to form colourless N_2O_4 molecules
—colourless, since each atom now has its full complement of electrons—

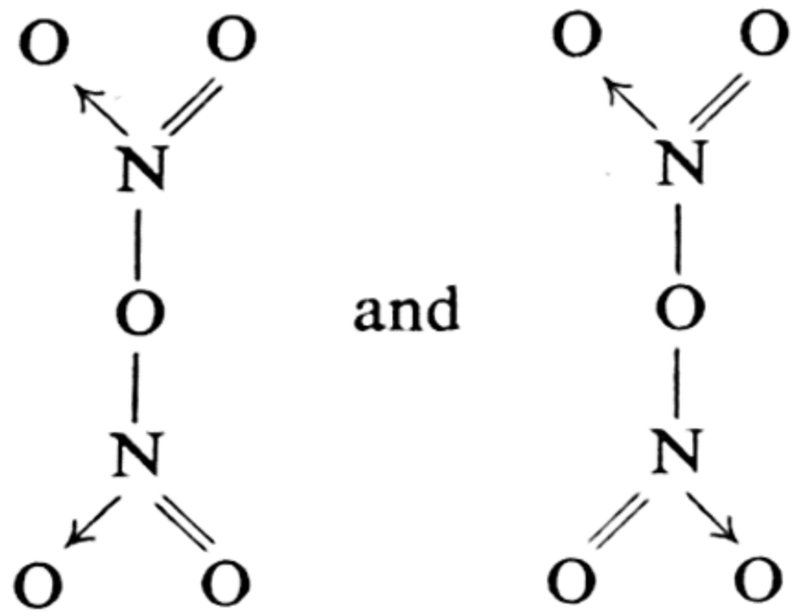


In the case of nitric oxide, the electron deficiency is associated neither with the oxygen atom nor with the nitrogen atom, and no association to form double molecules, N_2O_2, occurs. Before such association could occur, energy would have to be supplied to convert the resonance form into either $N{=}O$ or $N{\leftarrow}O$, and it seems probable that this energy increment is greater than the energy release on forming a double molecule. In other words, the resonance form represents a lower energy state than the hypothetical double molecule, N_2O_2. This difficulty of forcing an additional electron into the resonance structure probably also accounts for the absence of colour shown by the gas.

Nitrous oxide is a resonance hybrid of the structures—

$$N{\equiv}N{\rightarrow}O \text{ and } N{\leftarrow}N{=}O$$

and *nitric anhydride* (or, nitrogen pentoxide) of the structures—



The results of the resonance are those already discussed briefly in connexion with nitric oxide, results which apply generally to all cases of resonance structures.

Nitric Acid, HNO_3

Laboratory Preparation. When concentrated sulphuric acid is added to a nitrate, such as potassium nitrate, the following reversible reaction occurs—

$$KNO_3 + H_2SO_4 \rightleftharpoons KHSO_4 + HNO_3$$

If the mixture is heated, the more volatile nitric acid escapes so that the reaction becomes irreversible. A convenient form of apparatus in which to carry out this reaction and collect the nitric acid is shown in the accompanying diagram. The distillate is almost 100 per cent nitric acid but is coloured brown by dissolved nitrogen peroxide produced by the decomposition of some of the nitric acid. This dissolved oxide may be removed by blowing a current of dry air or nitrogen through the acid, preferably at about 60°C, or by adding a little urea—

$$2HNO_2 + CO(NH_2)_2 = CO_2 + 2N_2 + 3H_2O$$

It should be noted in connexion with this preparation that—

(*a*) The nitric acid is almost anhydrous, due to the dehydrating action of the concentrated sulphuric acid.

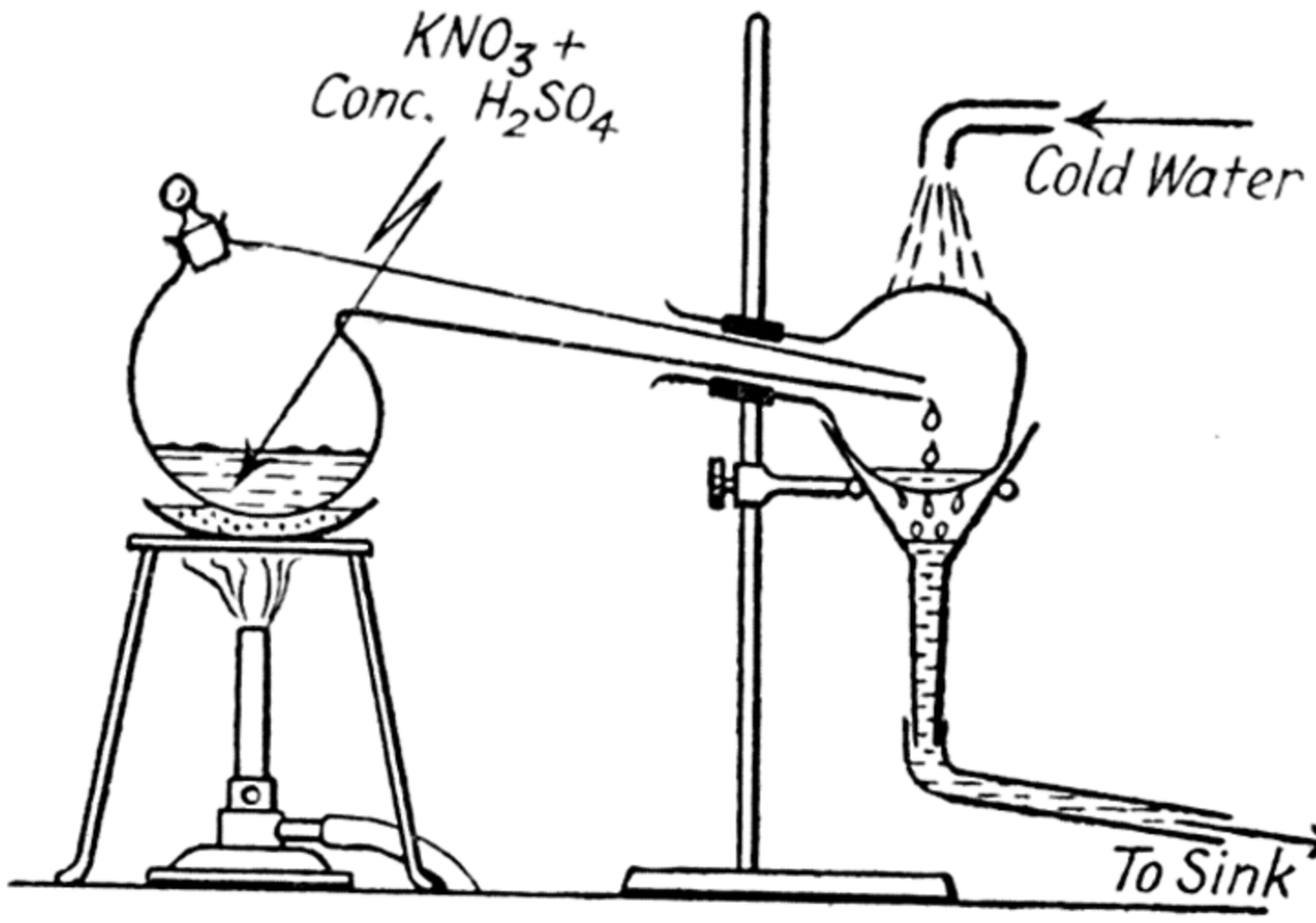


FIG. 209. Preparation of Nitric Acid

(*b*) A much higher temperature would be required for the complete reaction

$$2KNO_3 + H_2SO_4 = K_2SO_4 + 2HNO_3$$

and at such a temperature appreciable decomposition of the nitric acid would occur.

(*c*) The liberation of the nitric acid by the action of the sulphuric acid does not necessarily mean that the latter is the stronger acid. In the present reaction, it simply means that nitric acid has a lower boiling point (78° to 84°C as compared with 338° for sulphuric acid.)

On a commercial scale, nitric acid is produced (*a*) from natural nitrates such as Chile salt-petre; (*b*) by the Arc or Birkelande-Eyde Process (*see* p. 631) although this method is now largely replaced by (*c*) the Ammonia-Oxidation Process.

From Chile Saltpetre, $NaNO_3$. Nitric acid was formerly made almost entirely from sodium nitrate by reaction with concentrated sulphuric

acid, but nowadays the process is only carried out in areas conveniently connected, by sea or land, with the natural nitrate deposits. The process is performed in cast-iron retorts and the nitric acid condensed in cooling coils and collected in earthenware vessels, in a manner similar to that detailed in connexion with the laboratory preparation.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3 \uparrow$$

The reaction is usually stopped before all the sulphuric acid has been converted to the bisulphate, so that a liquid residue is obtained which may easily be run out of the retorts. This residue of sodium bisulphate, containing a little sulphuric acid, is known as nitre-cake, and was formerly extensively used to manufacture hydrochloric acid from common salt—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl \uparrow$$

From Ammonia. The bulk of the world's supply of nitric acid is nowadays obtained by the catalytic oxidation of ammonia, followed by solution of the resulting oxides of nitrogen in water. The essential reactions in the order in which they occur are—

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad . \quad . \quad . \quad (a)$$

$$2NO + O_2 = 2NO_2 \quad . \quad . \quad . \quad . \quad (b)$$

$$3NO_2 + H_2O = 2HNO_3 + NO \quad . \quad . \quad . \quad (c)$$

The oxidation of the ammonia is carried out by passing ammonia and excess of air (1:10 by volume) through a multilayered very fine rhodium-platinum gauze pad at a temperature of approximately 750°C. The catalyst pad may consist of from 18 to 24 platinum-rhodium gauzes (10 per cent Rh) and is clamped between a nickel ring and a Nichrome support. The gauzes are initially moistened with dilute nitric acid and heated in a slow stream of the hydrogen-nitrogen mixture by allowing a hydrogen flame to play on the pad. The flow of gases is then increased fairly rapidly until the plant is running at full capacity. The reaction occurs very rapidly, the mean contact time being of the order of 10^{-4} seconds. In practice the total weight of ammonia oxidized in a given time is increased by compressing the gases to about 100 lb/in.^{2} pressure. Increasing the pressure not only increases the rate of production of the nitric acid, but enables a 61–65 per cent acid to be obtained as compared with the 50–55 per cent acid obtained when the oxidation occurs at atmospheric pressure.

The conversion of the nitric oxide to nitrogen peroxide (reaction (*b*)) occurs relatively slowly and requires a lower temperature. The gases from the catalyst chamber are therefore cooled by passing through heat-interchangers and water-cooled coils before passing up large-capacity, stainless steel, absorption towers, provided with internal cooling coils,

in which the gases meet a descending spray of water. The capacity of this tower, or towers if several be used, is so arranged that the whole of the nitric oxide is ultimately converted into nitric acid—

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$
$$2NO + O_2 \rightarrow 2NO_2, \text{ etc.}$$

Concentration of Nitric Acid. When nitric acid solutions are boiled, the concentration increases by evaporation, until at 120·5°C/760 mm a 68 per cent nitric acid boils unchanged. This constant boiling mixture of

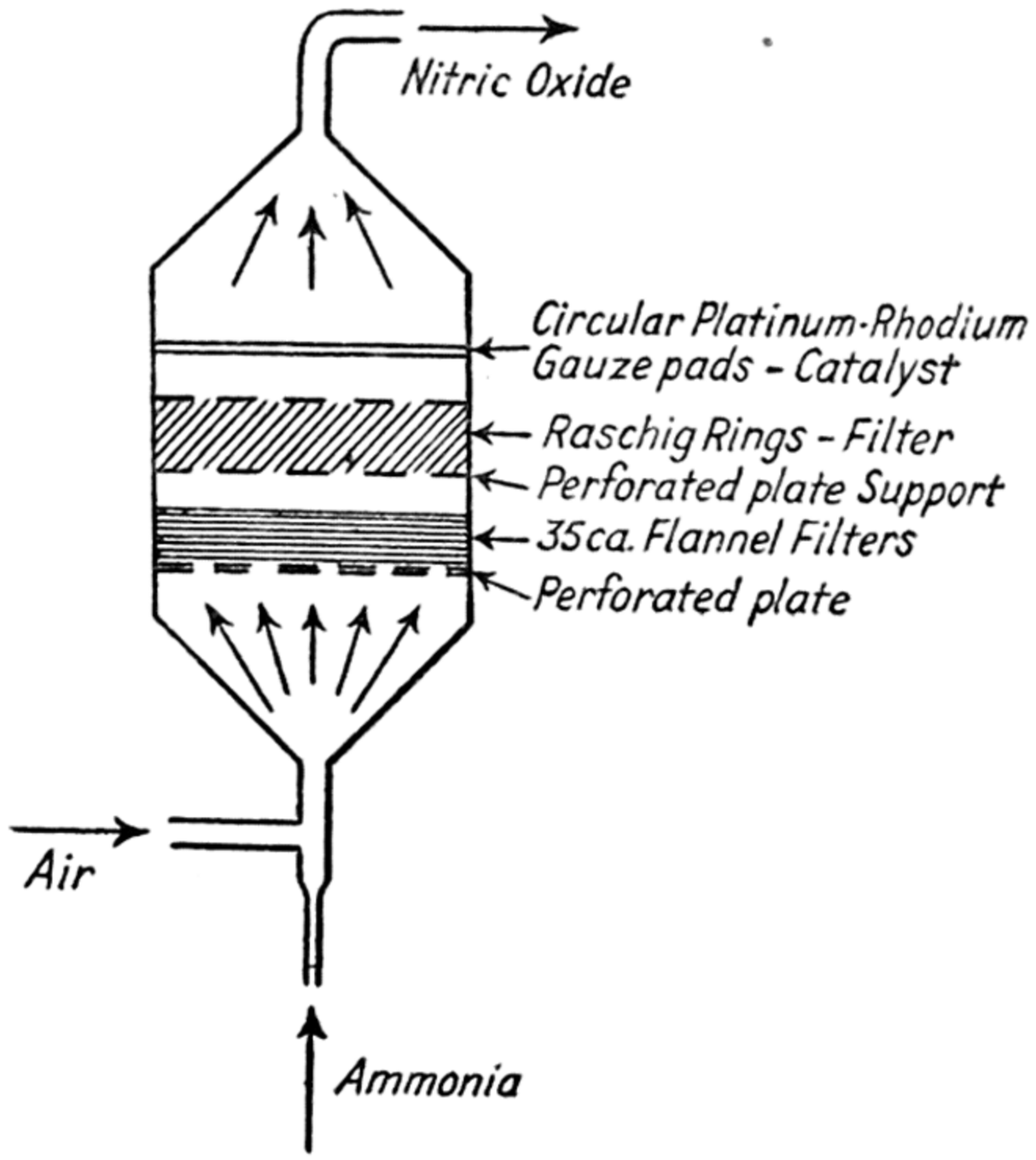


FIG. 210. Catalytic Oxidation of Ammonia in the Manufacture of Nitric Acid

nitric acid and water is the commercial concentrated nitric acid and has a specific gravity of 1·42. If more concentrated acid is required, for example as in the dyestuffs industry, advantage is taken of the dehydrating action of concentrated sulphuric acid. The concentration of the nitric acid distillate depends upon the strength of the sulphuric acid and on the distillation temperature. Concentrated sulphuric acid is fed into the top of a dehydrating tower, into the bottom of which is introduced the 68 per cent nitric acid and steam. The vapours evolved are progressively dehydrated in their passage up the towers, and pass over to the condensers to form the 98 per cent acid. Fuming nitric acid, sp. gr. 1·5, contains about 95 per cent nitric acid. The 100 per cent acid boils at 86°C.

Properties of Nitric Acid. Nitric acid is almost completely ionized in solution and is, therefore, like hydrochloric acid, a very strong acid. In

addition to its acidic properties, it is a powerful oxidizing agent and also, when concentrated, a nitrating agent in organic chemistry.

The acid decomposes on heating to liberate nitrogen peroxide and oxygen, and if the reaction be carried out by allowing the concentrated acid to drip slowly through the strongly heated stem of a church-warden clay-pipe, the oxygen may be collected—the nitrogen peroxide dissolving in the water.

$$4HNO_3 = O_2 + 4NO_2 + 2H_2O$$

The behaviour of nitric acid as an *oxidizing agent* is illustrated by such reactions as—

$$3H_2S + 2HNO_3 = 3S + 2NO\uparrow + 4H_2O$$
$$6HI + 2HNO_3 = 4H_2O + 3I_2 + 2NO\uparrow$$

both reactions occurring with the dilute acid at ordinary temperatures. Sulphur, phosphorus and iodine are oxidized to their respective oxy-acids on boiling with concentrated nitric acid—

$$S + 6HNO_3 = H_2SO_4 + 6NO_2\uparrow + 2H_2O$$
$$P + 5HNO_3 = H_3PO_4 + 5NO_2\uparrow + H_2O$$
$$I_2 + 10HNO_3 = 2HIO_3 + 10NO_2\uparrow + 4H_2O$$

It should be noted that nitrogen peroxide is evolved when concentrated nitric acid is used, and nitric oxide when a weaker acid is used. This is due to the effect of concentration on the equilibrium position of the reaction—

$$NO + 2HNO_3 \rightleftharpoons 3NO_2 + H_2O$$

The ability of aqua-regia (3 volumes concentrated HCl + 1 volume concentrated HNO_3) to dissolve the noble metal gold is due to the oxidation of the hydrochloric acid to liberate chlorine which converts the gold into auric chloride. The latter dissolves in excess of hydrochloric acid to form the soluble chlorauric acid, $HAuCl_4$—

$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O$$
$$2Au + 3Cl_2 = 2AuCl_3$$
$$AuCl_3 + HCl = HAuCl_4$$

Nitric acid will also oxidize ferrous salts to ferric salts, a reaction which is the basis of the brown-ring test for nitrates and also a method for preparing pure nitric oxide gas.

The reaction of *nitric acid on the metals* is particularly interesting in view of the number of different products that may be obtained. The only metals not attacked by the acid are the noble metals, gold, platinum, rhodium, etc., although certain other metals, such as iron and chromium,

become *passive* when treated with the strong acid. This passivity is thought to be due to the formation of an invisible, impermeable, protecting oxide film. The stainless steels and other chromium and nickel alloys are similarly not attacked by the acid, a property which accounts for their increasing use in the construction of nitric acid plant.

All the other metals react with nitric acid and the products of the reaction appear to be determined by—

(*a*) the reactivity of the metal, as determined by its position in the electro-chemical series (*see* p. 272), and

(*b*) the concentration of the nitric acid.

With *the metals above hydrogen* in the electro-chemical series, the primary reaction appears to be the liberation of nascent hydrogen which then reduces the nitric acid. The extent to which the nitric acid is reduced, as indicated by the following equations, is determined both by the speed of the primary reaction, that is the rate of formation of the nascent hydrogen, and by the number of nitric acid molecules present, that is its concentration.

$$HNO_3 + \overline{H} = H_2O + NO_2 \uparrow$$
$$HNO_3 + 3\overline{H} = 2H_2O + NO \uparrow$$
$$2HNO_3 + 8\overline{H} = 4H_2O + H_2N_2O_2 \rightarrow N_2O \uparrow + H_2O$$
$$HNO_3 + 6\overline{H} = 2H_2O + NH_2OH$$
$$HNO_3 + 8\overline{H} = 3H_2O + NH_3 \uparrow$$

These equations are representative of the many possible reactions that may occur and should not be regarded as covering all the possibilities.

With the very reactive *magnesium* metal and very dilute nitric acid, the rate of formation of nascent hydrogen so greatly exceeds the remaining available nitric acid molecules with which they might react, that the hydrogen escapes as a gas and may be collected.

$$Mg + 2HNO_3 = Mg(NO_3)_2 + H_2 \uparrow$$

With slightly more concentrated acid the balance is restored, and the main product is now ammonia, which is however neutralized by the excess acid to form ammonium nitrate.

With a slightly less reactive metal such as *zinc* or *aluminium* and hot dilute acid, no free hydrogen escapes, and the main product is again ammonium nitrate, but this may decompose at the temperature of the reaction to liberate nitrous oxide gas—

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$
$$NH_4NO_3 = N_2O \uparrow + 2H_2O$$

In general, it may be said that the more reactive the metal and the weaker

the nitric acid, the more complete is the reduction, and conversely the less reactive the metal and the more concentrated the acid the less is the reduction—

$$\xleftarrow{\text{Most reduction}} \quad NH_3,\ NH_2OH,\ N_2O,\ NO,\ NO_2 \quad \xrightarrow[\text{Least reduction}]{}$$

With the metals, such as *copper*, *silver* and *mercury* which are below hydrogen in the electro-chemical series, the primary reaction is probably an oxidation reaction. Veley (1890) showed that a small amount of nitrous acid or oxides of nitrogen must be present in the nitric acid before these metals will react, and this suggests that the primary reaction is—

$$Cu + 2HNO_2 = CuO + H_2O + 2NO\uparrow$$

or

$$Cu + NO_2 = CuO + NO\uparrow$$

Once started the reaction proceeds increasingly quickly due to the increasing temperature and to the increasing liberation of nitrogen peroxide by the reaction—

$$NO + 2HNO_3 = H_2O + 3NO_2\uparrow$$

in which the concentrated nitric acid oxidizes the nitric oxide to nitrogen peroxide. The latter reacts with the copper as above. The products of the reaction are thus cupric nitrate, formed by reaction of the copper oxide with the nitric acid, and nitric oxide or nitrogen peroxide gas, depending upon whether the nitric acid is moderately concentrated (50 per cent) or concentrated—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

With the less concentrated acid, the nitric oxide liberation results mainly from the reaction—

$$3NO_2 + H_2O = 2HNO_3 + NO\uparrow$$

and with the concentrated acid, the liberation of nitrogen peroxide from the reverse reaction—

$$2HNO_3 + NO = H_2O + 3NO_2\uparrow$$

This theory of the mode of reaction of nitric acid with the baser metals appears to be supported by the absence of other products of reduction, such as ammonia and nitrous oxide, and by the closely similar behaviour of the nitric oxide-nitrogen peroxide system in the manufacture of sulphuric acid by the Chamber Process—

$$H_2SO_3 + NO_2 = H_2SO_4 + NO\uparrow$$

Before concluding this section on the reaction of the metals with nitric acid, mention should be made of the behaviour of *tin*. With the anhydrous or very concentrated nitric acid, no reaction occurs. With the ordinary concentrated acid, no reaction appears to occur but may suddenly, after an appreciable interval, proceed with almost explosive violence. The experiment may be carried out by pouring some concentrated nitric acid on to powdered tin in a small beaker. After an interval, measured in tens of seconds, the reaction occurs somewhat violently to produce a cloud of brown nitrogen peroxide and leave a white residue of meta-stannic acid ($SnO_2 + H_2O$)—

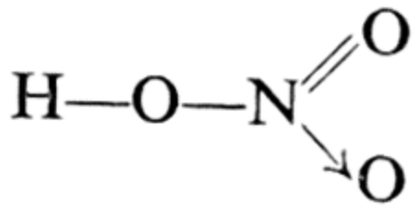
$$Sn + 4HNO_3 = H_2SnO_3 + 4NO_2\uparrow + H_2O$$

With less concentrated acid the reaction occurs on heating and the products are stannic nitrate, which hydrolyses to metastannic acid, and nitric oxide. When the nitric acid is cold and very dilute, the reaction is—

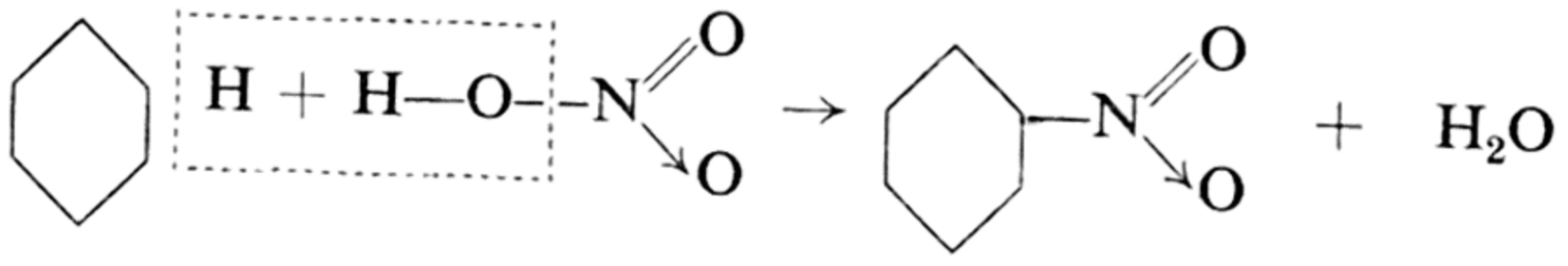
$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$$

and stannous nitrate is formed. On heating, the ammonium nitrate decomposes to liberate nitrous oxide.

Formula of Nitric Acid. The non-reaction of the 100 per cent acid on the metals and its use as a nitrating agent in organic chemistry suggests that it has the purely covalent structure



The conversion of benzene into nitro-benzene is typical of the nitration reactions, and probably occurs as follows—



Concentrated sulphuric acid is always mixed with the nitric acid in these reactions and was thought to react—

(i) by removing the water formed in the reaction, and
(ii) by converting a non-100 per cent nitric acid virtually into the 100 per cent acid by its powerful dehydrating action.

Recent work has shown, however, that the following reversible reaction occurs in the acid nitrating mixture—

$$HO \,.\, NO_2 + 2H_2SO_4 \rightleftharpoons (NO_2)^+ + (H_3O)^+ + 2HSO_4^-$$

and there is undisputable evidence that the effective nitrating agent is the positive nitronium ion, $(NO_2)^+$.

The slightly less concentrated nitric acid is thought to have the nitronium

nitrate structure, in which the hydrogen ion is *solvated* with a molecule of nitric acid—

$$HNO_3 = H^+ + NO_3^-$$

$$H^+ + H{-}O{-}NO_2 = \left[\begin{array}{l} H{-}O \\ \quad\quad\rangle N{=}O \\ H{-}O \end{array}\right]^+$$

that is,

$$\left[\begin{array}{l} H{-}O \\ \quad\quad\rangle N{=}O \\ H{-}O \end{array}\right]^+ \quad \left[\begin{array}{l} O \\ \quad\quad\rangle N{=}O \\ O \end{array}\right]^-$$

The still less concentrated acid has the normal ionic structure in which the hydrogen ion is solvated by a molecule of water forming the usual hydroxonium ion

$$HNO_3 + H_2O = (H_3O)^+ + (NO_3)^-$$

Action of Heat on Nitrates

(*a*) Ammonium nitrate decomposes to liberate nitrous oxide—

$$NH_4NO_3 = N_2O\uparrow + 2H_2O\uparrow$$

(*b*) Sodium and potassium nitrates on heating liberate oxygen and form the nitrite—

$$2NaNO_3 = 2NaNO_2 + O_2\uparrow$$

(*c*) Nitrates of magnesium, zinc, copper, etc., liberate nitrogen peroxide and oxygen, and form the oxide of the metal—

$$2Pb(NO_3)_2 = 2PbO + 4NO_2\uparrow + O_2\uparrow$$

(*d*) With the nitrates of the baser metals, such as mercury and silver, the oxide first formed decomposes to the metal—

$$Hg(NO_3)_2 = Hg + 2NO_2\uparrow + O_2\uparrow$$

Estimation of Nitric Acid and Nitrates. Free *nitric acid* may be determined by direct titration with a standard alkali following the normal procedure.

Nitrates (and nitrites) may be estimated by reduction to ammonia by Devarda's alloy (Cu, 50 per cent; Al, 45 per cent; Zn, 5 per cent) in alkaline solution. The nitrate is treated with Devarda's alloy in presence of sodium hydroxide, and the liberated ammonia absorbed in standard sulphuric acid. The excess of sulphuric acid is then determined by back titration.

$$NaNO_3 + 8\overline{H} = NaOH + NH_3\uparrow + 2H_2O$$

Small quantities of nitrates (and nitrites) may also be estimated by measuring the volume of nitric oxide liberated when they are treated with mercury and concentrated sulphuric acid—

$$6Hg + 2HNO_3 + 3H_2SO_4 = 3Hg_2SO_4 + 2NO\uparrow + 4H_2O$$

The determination is carried out in a Lunge nitrometer which consists of a graduated cylindrical tube, connected at its lower end with a mercury reservoir (the height of which may be varied so as to fill the graduated tube with mercury), and at its upper end, via a ground glass stop-tap, with a small cup through which are added the nitrate and sulphuric acid.

Nitrous Acid and Nitrites. When a solution of a nitrite is acidified *in the cold* a pale blue solution is obtained. This solution may contain some nitrous acid, but the blue colour is almost certainly due to the decomposition product of this acid, namely, nitrous anhydride N_2O_3.

$$2NaNO_2 + H_2SO_4 = Na_2SO_4 + 2HNO_2$$

$$2HNO_2 = H_2O + N_2O_3$$

Nitrous acid is very unstable and readily decomposes into its anhydride which in its turn dissociates into nitric oxide and nitrogen peroxide.

Nitrites are the salts of nitrous acid, and are much more stable than the acid. They may be prepared—

(*a*) By heating the nitrates of sodium or potassium in air.

(*b*) By heating the same nitrates with a little metallic lead—

$$NaNO_3 + Pb = NaNO_2 + PbO$$

(*c*) By distilling arsenious oxide with nitric acid and absorbing the mixture of nitric oxide and nitrogen peroxide in a suitable alkali under air-free conditions.

$$As_2O_3 + 2HNO_3 = As_2O_5 + NO\uparrow + NO_2\uparrow + H_2O$$

$$2KOH + NO_2 + NO = 2KNO_2 + H_2O$$

Properties of Nitrous Acid. Brown fumes of nitrogen peroxide are liberated when a nitrite is acidified, even by such a weak acid as acetic acid, due to the decomposition of the nitrous acid first formed.

If the nitrite is acidified in presence of urea, nitrogen is liberated—

$$CO(NH_2)_2 + 2HNO_2 = CO_2\uparrow + 3H_2O + 2N_2\uparrow$$

This reaction is often used to remove residual oxides of nitrogen from a solution, for example, in the removal of oxides of nitrogen from nitric acid, and also in the determination of copper. The copper is dissolved in nitric acid, and the excess acid removed by evaporating and neutralizing. Any residual oxides of nitrogen, which would interfere with the subsequent potassium iodide-thiosulphate estimation, are then removed by adding a little urea and boiling.

Nitrous acid (that is, acidified nitrites) reacts at ordinary temperature both as an oxidizing agent and as a reducing agent.

Oxidizing Action of Nitrous Acid. It is more reactive than nitric acid, and, for example, will immediately liberate iodine from hydriodic acid.

The reaction is carried out by adding a nitrite to acidified potassium iodide—

$$2KNO_2 + 2KI + 2H_2SO_4 = 2K_2SO_4 + I_2 + 2NO\uparrow + 2H_2O$$

In all the reactions in which nitrous acid behaves as an oxidizing agent, nitric oxide is liberated, as indicated by the basic equation—

$$2HNO_2 \rightarrow H_2O + 2NO + \overline{O}$$

The O is, of course, not liberated and should be regarded only as a measure of the oxidizing power of two molecules of nitrous acid. It should be noted that the same equations are obtained if the active oxidizing agent is considered to be the nitrogen peroxide liberated by decomposition of nitrous acid—

$$2HNO_2 \rightarrow H_2O + NO + NO_2 \rightarrow H_2O + 2NO + \overline{O}$$

Other examples of the oxidizing action of nitrous acid include the conversion of stannous chloride to stannic chloride, ferrous salts to ferric salts, sulphuretted hydrogen to sulphur and sulphurous acid to sulphuric acid, the latter reaction recalling the behaviour of the oxides of nitrogen in the Chamber Process. In all these reactions nitric oxide is liberated.

Reducing Action of Nitrous Acid. Nitrous acid is easily oxidized to nitric acid—

$$HNO_2 + \overline{O} \rightarrow HNO_3$$

and so may also be regarded as a reducing agent. Thus, nitrous acid is oxidized by acidified permanganate and dichromate solutions, bromine water and by chlorine water—

$$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = 5KNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

$$HNO_2 + Br_2 + H_2O = HNO_3 + 2HBr$$

Formula of Nitrous Acid. The very weak acidic nature of the acid indicates that it is mainly non-ionized, and has a covalent structure. Two such structures appear possible—

$$H—O—N=O \quad \text{and} \quad H—N\begin{matrix}=O\\ \searrow O\end{matrix}$$

The behaviour of the acid in certain organic reactions suggests that both of these structures occur in equilibrium.

Hyponitrous Acid, $H_2N_2O_2$. This acid is very unstable, and decomposes on exposure to the air to form nitric and nitrous acids—

$$2H_2N_2O_2 + 3O_2 = 2HNO_2 + 2HNO_3$$

The aqueous solution may be prepared by the action of hydroxylamine

on a nitrite in the presence of an acid. On warming, the hyponitrous acid decomposes to liberate nitrous oxide, N_2O—

$$H—O—N\boxed{H_2 + O}N—O—H = \boxed{H-\boxed{-O—N=N-}-O—H} \rightarrow N_2O + H_2O$$

PHOSPHORUS

Phosphorus occurs immediately below nitrogen in Group V of the Periodic Classification—

Nitrogen—Phosphorus { Niobium—Tantalum—Protoactinium / Arsenic—Antimony—Bismuth

It is a non-metal and was first isolated in very small quantities by Brand of Hamburg in 1674, who obtained it by strongly heating evaporated urine with sand. The name phosphorus was later suggested for the element because of its property of glowing in the dark, whilst the term "phosphor" is retained as a generic name for a large class of substances which do not contain phosphorus but which are also luminescent, such as commercial calcium and barium sulphides. Long before phosphorus was discovered however, certain natural products, such as bird dung, guano, fish and bones were much prized as fertilizers. It is now known that the active constituents of these natural materials contain phosphorus in the form of phosphates, and today considerable quantities of phosphates are manufactured and used for fertilizer purposes. It was not, however, until 1771 that Scheele isolated phosphorus from bone-ash and so opened the way to the production of the element and its compounds on a commercial scale.

Occurrence. Phosphorus does not occur free in nature. It is an essential constituent of animal and vegetable tissues, and large quantities occur, as calcium phosphate, $Ca_3(PO_4)_2$, in bones. Most of the phosphorus and its compounds manufactured today are, however, obtained from the mineral phosphates, or phosphate rocks, of which the most important are *Apatite* minerals, and include—

Fluorapatite, $CaF_2 . 3Ca_3(PO_4)_2$
Chlorapatite, $CaCl_2 . 3Ca_3(PO_4)_2$
Sombrerite, $Ca_3(PO_4)_2$
Wavellite, $2AlPO_4 . 2Al(OH)_3 . 9H_2O$

deposits of which occur principally in North Africa, Florida, the Pacific Islands, and in Russia.

Manufacture of Phosphorus. The original process, now mainly obsolete, obtained the phosphorus from bones. The latter were first degreased by digesting with organic solvents (benzene, etc.) and then boiled with water

under pressure to dissolve out the valuable gelatine. The bones were then destructively distilled to leave a residue of *bone-ash*, which is mainly calcium phosphate. The latter was then treated with chamber sulphuric acid (about 65 per cent strength) to form a solution of phosphoric acid—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4\downarrow + 2H_3PO_4$$

The phosphoric acid was then filtered off and partially evaporated. Charcoal or coke was then added and the mixture heated until the moisture

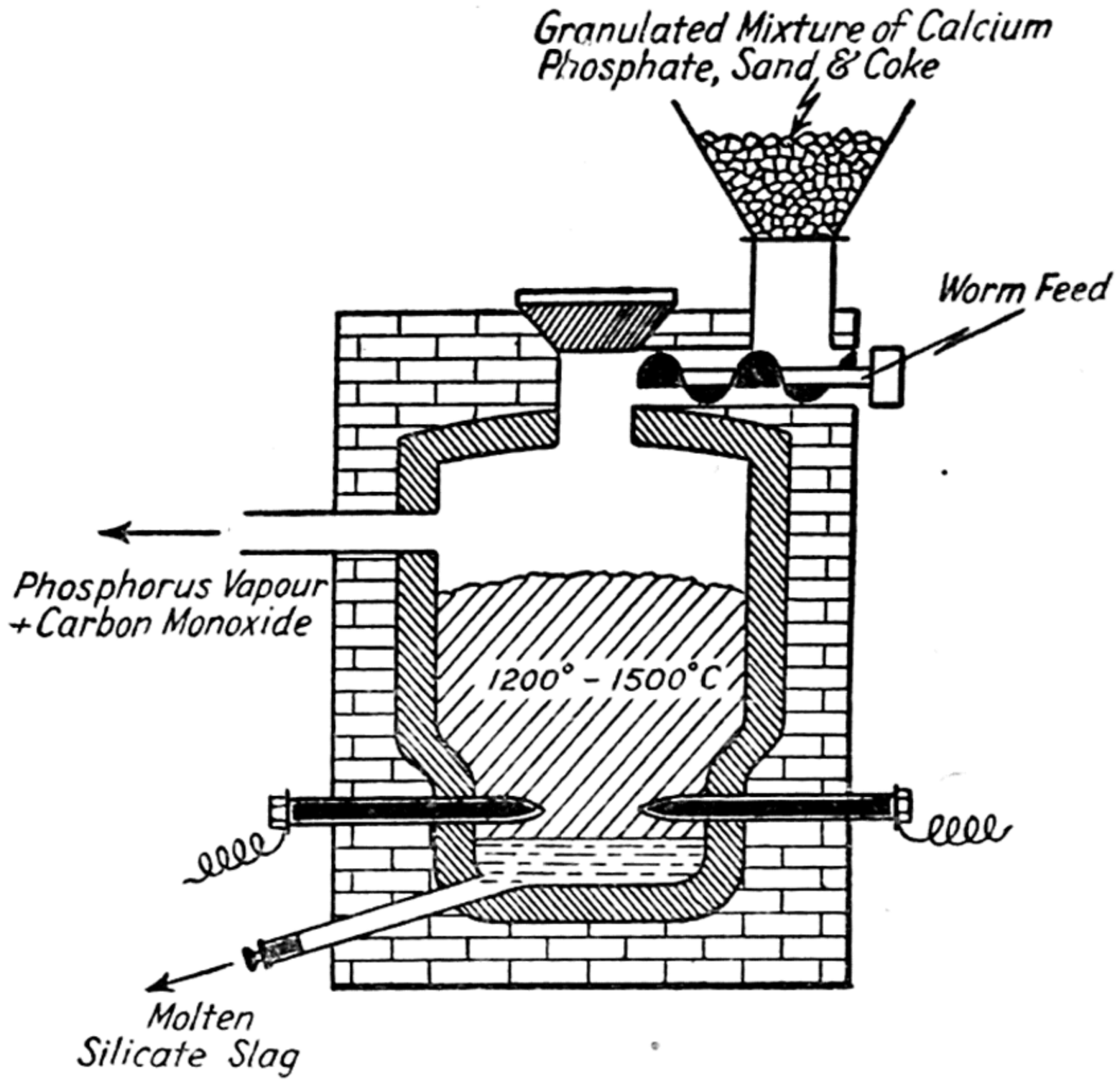


FIG. 211. Manufacture of White Phosphorus

content had been reduced to about 6 per cent or less, at which stage the phosphoric acid existed as the meta-acid—

$$\underset{\text{ortho-phosphoric acid}}{H_3PO_4} - H_2O = \underset{\text{meta-phosphoric acid}}{HPO_3}$$

The mixture was then transferred to retorts and heated to white heat, when the following reaction occurred with the previously added carbon—

$$2HPO_3 + 6C = 2P\uparrow + H_2\uparrow + 6CO$$

The phosphorus distilled over and was condensed under water. It was then purified by redistillation in an inert atmosphere.

Nowadays, phosphorus is produced in an electric furnace by a continuous process. The well-ground mineral phosphate is mixed with carbon and silica (sand), and the whole roughly granulated or sintered together before charging via the hopper and worm-feed into the furnace. This preliminary treatment ensures intimate contact between the reacting materials without unduly impeding the subsequent escape of phosphorus vapour. The furnace, shown diagrammatically on p. 670, consists of an iron tank lined inside with refractory bricks and provided with two massive carbon electrodes. When the charge is in position, the current is switched on and the temperature inside the furnace raised to between 1200° and 1500°C. The following reactions occur—

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$$

$$P_2O_5 + 5C = 2P\uparrow + 5CO\uparrow$$

In the first of these reactions, the more refractory silica is regarded as displacing the more volatile phosphorus pentoxide from its compound with calcium oxide. In the second reaction this phosphorus pentoxide is then reduced by the carbon to form carbon monoxide and liberate phosphorus. At the high temperature of the furnace the calcium silicate forms a molten slag which collects at the bottom and is periodically tapped. The phosphorus vapour which passes out of the furnace is condensed under water and the carbon monoxide which passes on is collected and used as a gaseous fuel. The crude phosphorus is then purified by melting under water (m.p. 44·5°C) and adding an acidified 4 per cent solution of sodium dichromate. After several hours, the phosphorus is separated, washed with hot water, filtered through canvas bags, and finally cast in the familiar stick form or block form for packing under water in sealed tins. The product is very pale yellow in colour and is variously referred to as either *White Phosphorus* (W.P.) or *Yellow Phosphorus* (Y.P.).

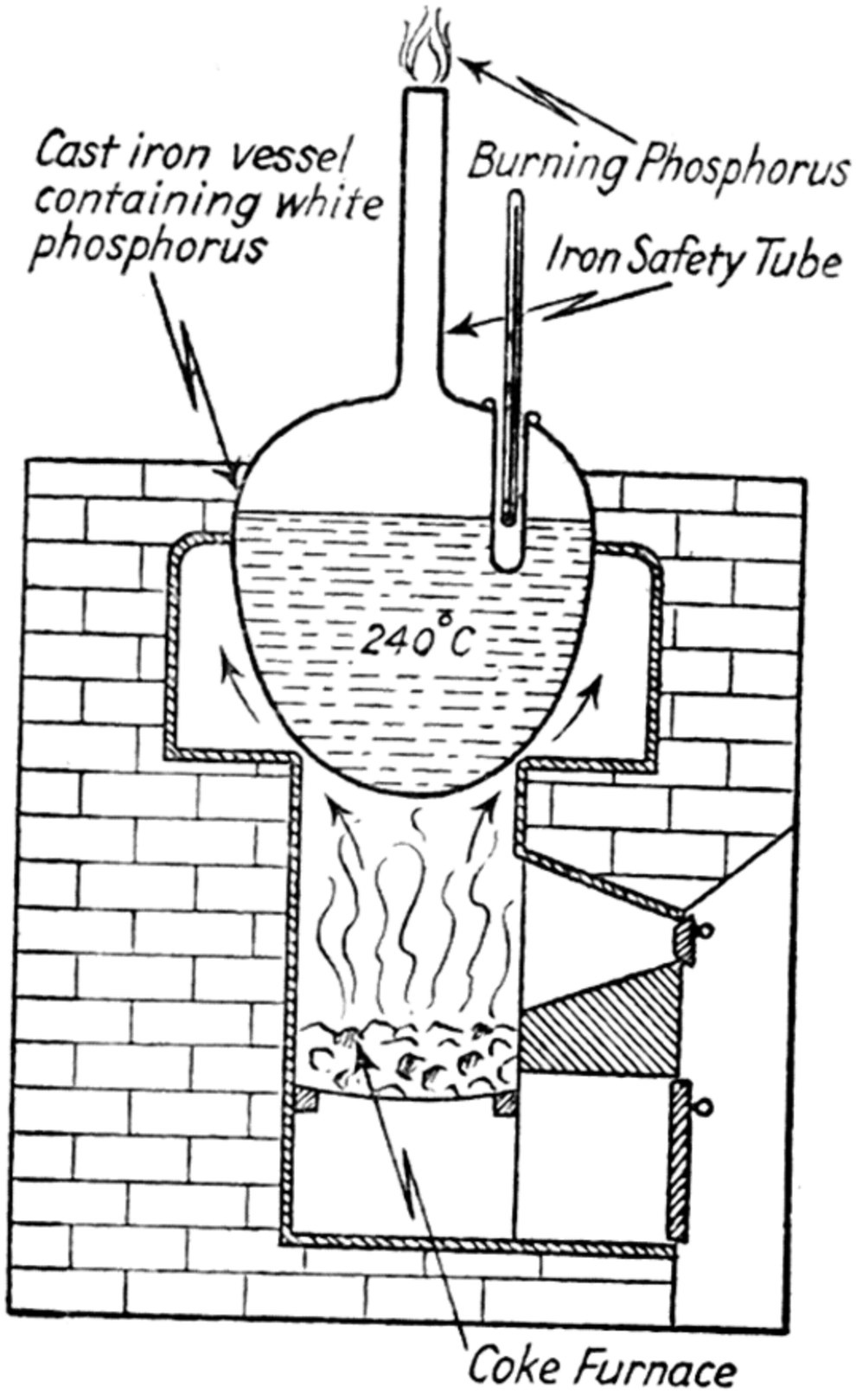


FIG. 212. Manufacture of Red Phosphorus

Red Phosphorus. This amorphous variety of phosphorus is manufactured by heating white phosphorus for several days (about eight) at about 240° to 250°C in a cast-iron vessel from which air is excluded. The change from white to red phosphorus occurs extremely slowly at ordinary temperatures,

but this rate is increased both by increasing the temperature and by the presence of catalysts, such as iodine, selenium and phosphorus tribromide; the temperature 240°–250°C represents a practical upper limit for the change. The resulting red phosphorus is then freed from any residual white phosphorus and any oxides of phosphorus by heating with an aqueous solution of sodium hydroxide; the latter reacts with any remaining white phosphorus, but not with red phosphorus, to form phosphine and sodium hypophosphite.

Allotropy of Phosphorus

White Phosphorus. Two forms of white phosphorus are known, the α-white phosphorus or ordinary white phosphorus, and the β-white phosphorus, discovered by Bridgman, which is stable below $-77°C$. These two forms of white phosphorus are enantiotropic (*see* p. 163) with a transition temperature at $-77°C$.

Violet Phosphorus (or, Hittorf's metallic phosphorus). The so-called red phosphorus, prepared as above, becomes increasingly violet when heated to a higher temperature for long periods, and it is now generally considered to be a solid solution or mixture of white and violet phosphorus.

$$\underbrace{\qquad\qquad}_{\text{Red Phosphorus}}$$
$$P_{white} \rightleftharpoons P_{violet}$$

TABLE 96

Allotropic Forms of Phosphorus

	α-White	β-White	Violet	Black
Preparation . .	By condensing phosphorus vapour under water	By action of high pressure on W.P.	By heating W.P. to 500° in lead for some hours	By high pressure compression (35 000 atm) of W.P.
Crystal form .	Cubic	Hexagonal	—	—
Density . .	1·85	1·8	2·3	2·7
Melting point .	44·1°C	—	620°C	—
Ignition temperature . . .	30°C (approx.)		260°C (approx.)	
Electrical conductivity . . .	Nil	Nil	Nil	Conductor
Solubility in carbon disulphide .	Good	—	Insoluble	Insoluble

The pure violet phosphorus may be prepared by heating a solution of phosphorus in lead to about 500°C for some ten hours in the absence of air. By subsequently dissolving away the lead with acids, the violet phosphorus is obtained as violet crystals.

Black Phosphorus. This recently discovered allotropic form of phosphorus is prepared by the action of very high pressures on white phosphorus. Thus Bridgman obtained it by compressing white phosphorus at ordinary temperature under a pressure of 35 000 atmospheres.

The relationship between these allotropic forms of phosphorus is most clearly seen in the vapour pressure-temperature diagram, Fig. 213. The curve *AB* is the vapour pressure curve for the solid violet phosphorus, and curve *BC* the vapour pressure curve for liquid phosphorus; violet phosphorus therefore melts at *B* (590°C).

The curves *GF* and *FE* are similarly the vapour pressure curves for the β-white phosphorus and the α-white phosphorus respectively, the temperature of intersection of these curves giving the transition temperature as − 77°C for the enantiotropic change—

β-white phosphorus ⇌ α-white phosphorus

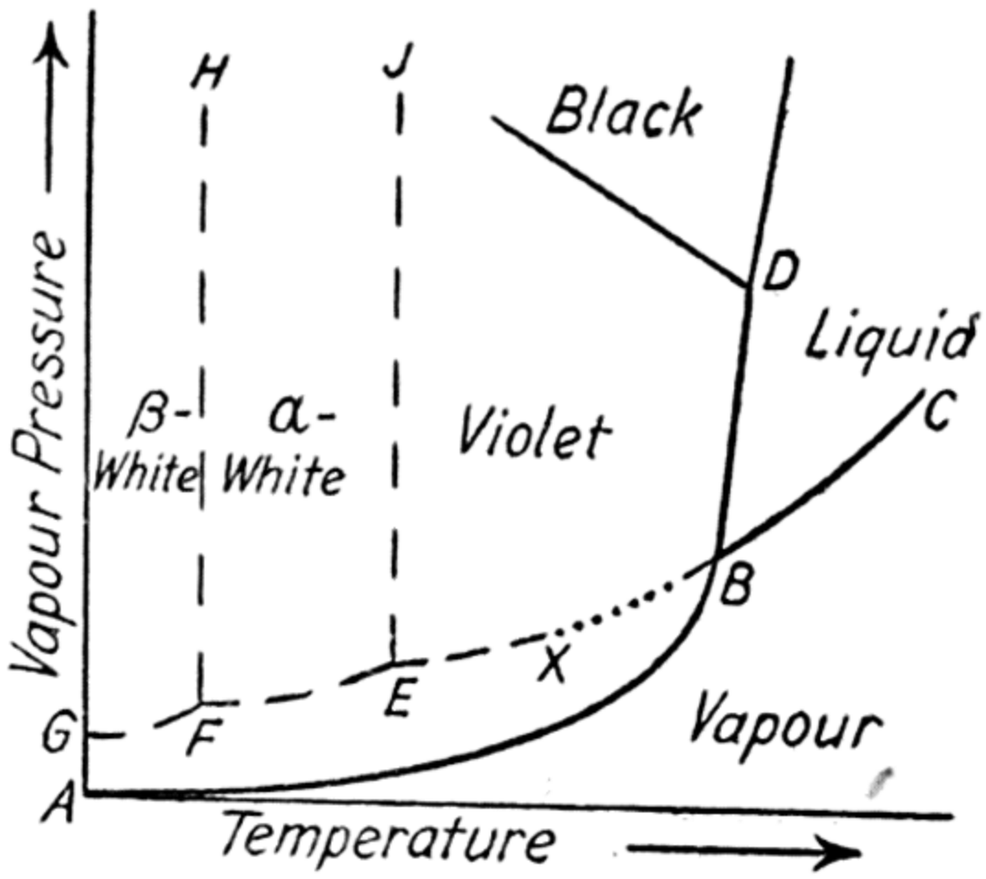


FIG. 213. Phosphorus Equilibrium Diagram

At *E*, white phosphorus melts, and the vapour pressure of the liquid white phosphorus then follows the curve *EX*. It has been shown experimentally that this curve, *EX* is continuous with the curve *BC*, and this fact suggests that ordinary white phosphorus is supercooled violet phosphorus.

The curves *FH*, *EJ* and *BD* show the effect of increasing pressures on the respective changes which occur at *F*, *E* and *B*; for example, the melting point of violet phosphorus increases slightly with increase in pressure. At very high pressures black phosphorus forms, and this change is shown in the upper portion of the vapour pressure diagram.

For practical purposes, however, it is only necessary to consider the two commercially available forms of phosphorus, white phosphorus and the less definite red phosphorus. If we take the vapour pressure curve of violet phosphorus to represent that of red phosphorus, then it is seen that—

(*a*) The vapour pressure of white phosphorus is greater than that of red phosphorus at all temperatures.

(*b*) The two vapour pressure curves do not intersect below the melting point, so that there is no transition temperature for a reversible change of white to red phosphorus.

These observations show that white phosphorus is in a metastable state at all temperatures up to the melting point of red phosphorus, and that the latter is the stable form. This type of allotropy in which there is no transition temperature, and in which one form is always in the metastable state is often referred to as *Monotropic Allotropy*. The results of the higher vapour pressure and hence increased energy content of white phosphorus are briefly—

(i) White phosphorus is very much more reactive than red phosphorus.
(ii) White phosphorus has a lower density than red phosphorus.
(iii) White phosphorus is soluble in many organic solvents whereas red phosphorus is not.
(iv) The change white phosphorus → red phosphorus will tend to occur spontaneously at all temperatures up to the melting point of red phosphorus, but the speed of this change will naturally be increased by increasing the temperature, and by the presence of catalysts.

TABLE 97

Properties of White and Red Phosphorus

Property	White Phosphorus	Red Phosphorus
Melting point	44·5°C	620°C (under pressure)
Specific gravity	1·83	2·05–2·39
Smell	Garlic-like	Odourless
Solubility in—		
(*a*) water	Nil	Nil
(*b*) carbon disulphide	Soluble	Nil
(*c*) benzene	Slightly	Nil
Ignition temperature	30°C (approx.)	260°C (approx.)
Behaviour in air	Phosphoresces	Does not phosphoresce
Action on chlorine	Spontaneous reaction at ordinary temp.	Requires heat
Aqueous sodium hydroxide	Dissolves in the hot solution to form PH_3 and NaH_2PO_2	Insoluble
General remarks	Very active and very poisonous	Little reactivity and not poisonous

(v) The reverse change, red phosphorus → white phosphorus can only be carried out by converting the red phosphorus into the vapour and then condensing the vapour. This follows a natural law which in effect states that when a substance can exist in various states, each with different energy content, then the change of the substance in the highest energy

state to that having the lowest energy content occurs step-wise through the intermediate states. In the present instance, phosphorus vapour represents the highest energy state and on condensation forms white phosphorus, the state having the next highest energy content.

These differences between white and red phosphorus may be summarized with reference to the more important properties in the table shown opposite.

Because of its very low ignition temperature, white phosphorus is always stored under water. On no account should white phosphorus be handled, since it would soon ignite and produce very serious and painful burns, which even when properly treated require a long time to heal. The use of white phosphorus in various anti-personnel bombs and shells emphasizes the care with which white phosphorus must be treated.

If a phosphorus burn is obtained, the affected part should be immersed first in a solution of copper sulphate and then any phosphorus remaining in the wound removed with a pair of forceps. An alkaline solution, such as sodium carbonate, is then used to neutralize the phosphorus acids present in the wound.

When white phosphorus is exposed to the air in the dark it emits a pale greenish light and is said to phosphoresce. The phenomenon may also be observed when water to which a little white phosphorus has been added is distilled in the dark; the vapours are strongly phosphorescent. No simple explanation of the phenomenon has been given except that it is some form of oxidation reaction, in agreement with the fact that the phosphorus is slowly converted into one or other of its oxides. Probably something more complicated is involved since the glow only occurs if the oxygen is below a certain critical pressure, and even then the reaction is inhibited if traces of gases which destroy ozone, such as ethylene, sulphuretted hydrogen, etc., be present, or if the phosphorus be much below 0°C.

Other reactions of white phosphorus include—

(*a*) Its ability to combine directly with many metals to form phosphides. Thus if small quantities of sodium be cautiously warmed with phosphorus, combination occurs suddenly with a bright flash and sodium phosphide is formed. Other important phosphides include calcium phosphide, Ca_3P_2, and iron phosphide, Fe_3P. The sodium and calcium phosphides decompose with water to liberate phosphine, PH_3.

(*b*) Its powerful reducing properties, as illustrated by the precipitation of copper from solutions of copper salts (the copper coats the phosphorus), and its reaction with nitric acid to form ortho-phosphoric acid.

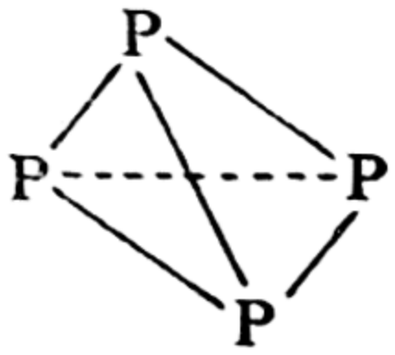
(*c*) Its ready reactivity with the non-metals, such as oxygen, chlorine and sulphur, details of which are given below in connexion with the compounds of phosphorus.

Uses of Phosphorus

(1) Most of the phosphorus produced is converted into the compounds such as phosphoric acid, various phosphates, pyrophosphates and meta-phosphates, the most important of which are summarized with their uses on p. 688.

(2) Yellow phosphorus was formerly used in the manufacture of matches but the high incidence of "phossy-jaw," a disease in which the phosphorus attacks the jaw-bones, led to its use for this purpose being banned, and a phosphorus sulphide, P_4S_3, is used instead. The head of the match usually contains the sulphide, P_4S_3, an oxidizing agent (e.g. MnO_2, $KClO_3$, etc.), glue, powdered glass, and a suitable dye (e.g. prussian blue, chrome yellow, etc.). Safety matches on the other hand contain an oxidizing agent, a fuel (antimony sulphide and sulphur or charcoal) but no phosphorus compound; the box usually contains red phosphorus and antimony sulphide.

(3) White phosphorus finds considerable use in war-time in smoke bombs, although its use in this connexion is limited by its tendency to "pillar"—the rapid combustion of the phosphorus produces a very dense cloud of white smoke consisting of the pentoxide, but this cloud tends to rise into the atmosphere rather than spread out on the ground. It is also used in anti-personnel weapons, and in certain petrol and benzene incendiary bombs as an igniting agent.



Formula of Phosphorus. At moderate temperatures, phosphorus in the solid and vapour states has the molecular formula P_4 in which the phosphorus atoms are arranged at the corners of a tetrahedron.

At higher temperatures, above 700°C, dissociation to P_2 occurs.

Compounds of Phosphorus

Hydrides. Three hydrides of phosphorus are known, phosphine, PH_3 (gas), diphosphine, P_2H_4 (liquid) and a less definite solid form, $P_{12}H_6$.

Phosphine, PH_3. The usual method for preparing phosphine in the laboratory is to boil a mixture of aqueous sodium hydroxide and white phosphorus, when the following reaction occurs—

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3 \uparrow$$

A solution of sodium hypophosphite is formed and phosphine gas liberated. A suitable form of apparatus is shown in the diagram. Coal gas, or other inert gas, is first passed through the apparatus to displace the air, because the small quantities of diphosphine, P_2H_4, produced at the same time makes the phosphine spontaneously inflammable. As each bubble of the impure phosphine breaks the surface of the water in the trough, it burns with a slight explosion and flash to produce rings of white smoke consisting of phosphorus pentoxide. If, however, the inflammable P_2H_4 be removed

by passing the impure phosphine through a tube immersed in a freezing mixture, the gas no longer inflames on coming into contact with the air, since the pure phosphine is not spontaneously inflammable.

Other methods of preparing phosphine include—

(*a*) The action of water on calcium phosphide—

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3 \uparrow$$

This reaction is put to practical use in the manufacture of various sea-markers designed for signalling purposes at night. The canister usually contains both calcium phosphide and calcium carbide. With water these

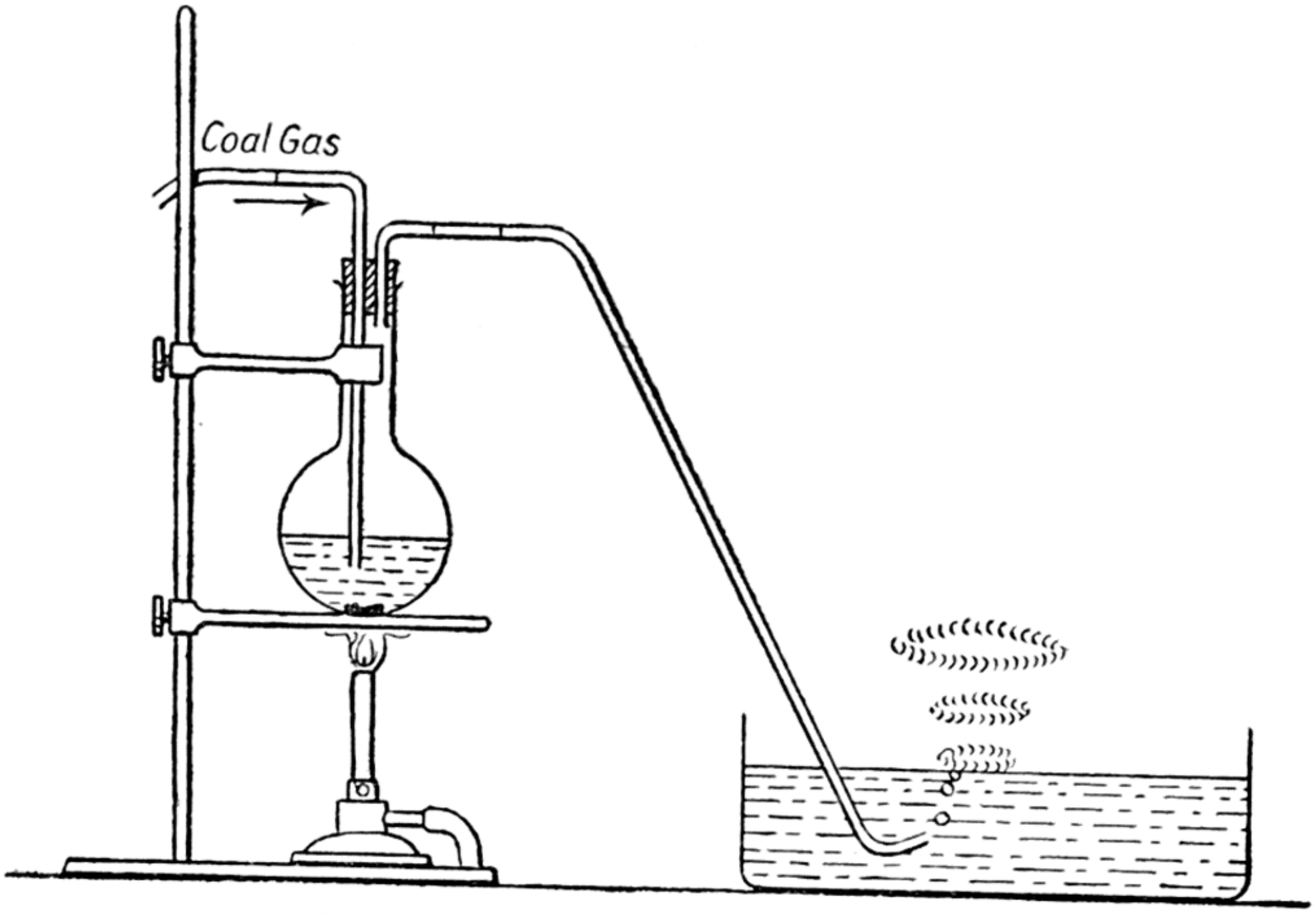


FIG. 214. Preparation of Phosphine

produce impure phosphine (spontaneously inflammable) and acetylene; the former ignites the acetylene as it escapes from the top of the floating canister.

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2 \uparrow$$

(*b*) Pure phosphine may be prepared by the action of sodium hydroxide on phosphonium iodide, PH_4I—

$$PH_4I + NaOH = PH_3 \uparrow + NaI + H_2O$$

This reaction recalls the method for preparing ammonia by the action of sodium hydroxide on an ammonium salt. The phosphonium iodide is made by dissolving phosphorus and iodine in carbon disulphide, carefully distilling off the latter, and then adding the calculated quantity of water as indicated by the equation—

$$5I + 9P + 16H_2O = 5PH_4I + 4H_3PO_4$$

The phosphonium iodide is then separated by sublimation in an atmosphere of carbon dioxide.

(*c*) Phosphine is liberated when the lower acids of phosphorus are heated. Thus when phosphorous acid is heated the oxidation of some of the molecules to phosphoric acid at the expense of other molecules results in the formation of phosphine—

$$4H_3PO_3 = PH_3\uparrow + 3H_3PO_4$$

Properties of Phosphine. Phosphine is a colourless, very poisonous gas which smells like decaying fish. It is only slightly soluble in water, but the resulting solution is not alkaline like aqueous ammonia and decomposes on standing to deposit red phosphorus. Phosphine burns vigorously in air to form phosphoric oxide, but when pure it is not spontaneously inflammable—

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O$$

Phosphine is a powerful reducing agent and will precipitate copper, silver and gold (or their phosphides) when passed through solutions of their salts.

TABLE 98

Comparison of Properties of Phosphine and Ammonia

Phosphine	Ammonia
Colourless gas with a fish-like odour	Colourless gas with a pungent (ammoniacal) odour
Very poisonous	Poisonous
Burns in air to form phosphorus pentoxide	Burns in oxygen to form nitric oxide
Very feebly soluble in water and solution is mainly neutral	Extremely soluble in water to form ammonium hydroxide
Powerful reducing agent e.g. $CuSO_4 \rightarrow Cu$	Reducing properties only develop in the hot; e.g. NH_3 passed over heated $CuO \rightarrow Cu$
Forms phosphonium compounds with difficulty, and these decompose with water	Forms ammonium salts easily and these dissolve in water without decomposition
P_2H_4, diphosphine known. It is solid and spontaneously inflammable	N_2H_4, hydrazine. Liquid, powerful reducing agent

Phosphonium Compounds. The most important of these is phosphonium iodide, PH_4I, the preparation of which is described above. Other phosphonium compounds include PH_4Cl and PH_4Br, and may be prepared by mixing dry phosphine with dry hydrogen chloride (or HBr) under pressure.

$$PH_3 + HCl = PH_4Cl$$

Since phosphorus and nitrogen occur in the same group of the Periodic Table, some similarity in the properties of phosphine and ammonia might be expected. The table on p. 678 shows the main differences and limited similarity between these two hydrides and their compounds.

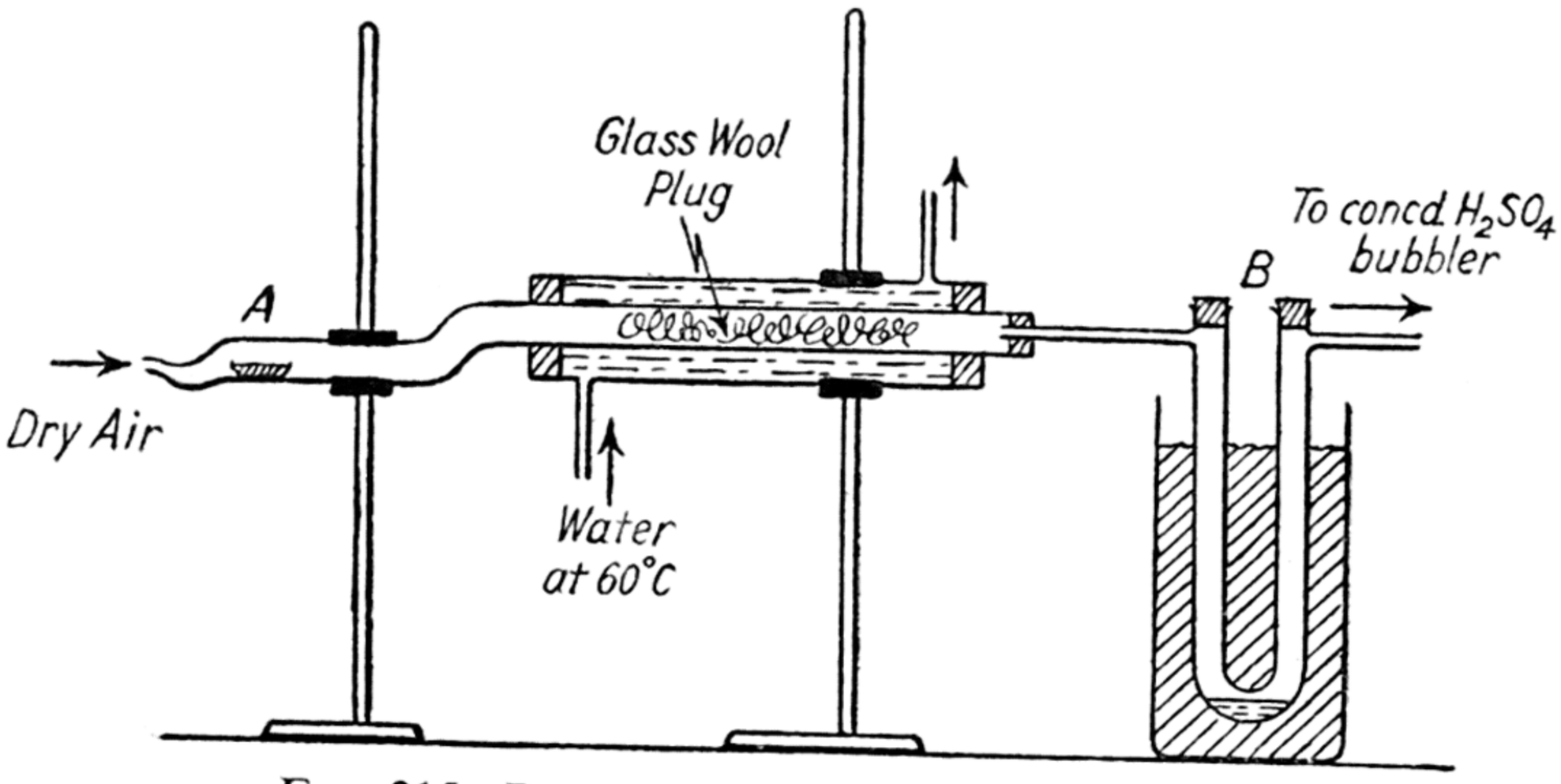


FIG. 215. Preparation of Phosphorus Trioxide

Oxides and Oxy-acids of Phosphorus. The principal oxides and oxy-acids of phosphorus are summarized in the following table—

Oxide	*Acid*
Phosphorus trioxide, P_4O_6	Hypophosphorous acid, H_3PO_2 Phosphorous acid, H_3PO_3
Phosphorus dioxide, P_4O_8	Hypophosphoric acid $H_4P_2O_6$
Phosphoric oxide, or phosphorus pentoxide, P_4O_{10}	ortho-Phosphoric acid, H_3PO_4 meta-Phosphoric acid, HPO_3 pyro-Phosphoric, $H_4P_2O_7$

Phosphorous Oxide or Phosphorus Trioxide may be prepared by burning phosphorus in a limited supply of air. A suitable form of apparatus is shown in the diagram. A slow stream of air is passed over gently heated white phosphorus contained in *A*, and the phosphorus pentoxide which is formed at the same time is removed by passing the gases through a water cooled tube (at about 60°C) containing a plug of glass wool. The latter serves to filter out any remaining uncondensed pentoxide. The trioxide passes on and condenses to a white solid in the U-tube *B* immersed in a

freezing mixture. A concentrated sulphuric acid bubbler which completes the train prevents moisture diffusing back from the air to the trioxide.

Phosphorus trioxide has a garlic-like odour and is poisonous. It is a white solid, melting point 23°C and boiling point 173°C. Slow oxidation to the pentoxide occurs on exposure to the air at ordinary temperature, but in warm oxygen the phosphorus trioxide may ignite. Phosphorus trioxide dissolves slowly in cold water to form phosphorous acid, H_3PO_3.

$$P_4O_6 + 6H_2O = 4H_3PO_3$$

but with hot water, phosphine and phosphoric acid are formed, due to the decomposition of the phosphorous acid.

$$4H_3PO_3 = PH_3 + 3H_3PO_4$$

Phosphorus Dioxide, P_4O_8. The separate existence of this oxide is now established. It may be obtained by heating phosphorus trioxide in a sealed tube at 440°C, and when dissolved in water forms a mixture of phosphorous and phosphoric acids

$$P_4O_8 + 6H_2O = 2H_3PO_3 + 2H_3PO_4$$

Phosphoric Oxide, or Phosphorus Pentoxide, P_4O_{10}. This oxide is formed when phosphorus burns in excess of dried air or oxygen. It is a white powder which sublimes on heating, very slowly at 50°C but more rapidly at higher temperatures. Its most remarkable property is its very great affinity for water. Thus it dissolves in water with a hissing noise with considerable evolution of heat to form meta-phosphoric acid—

$$P_4O_{10} + 2H_2O = 4HPO_3$$

With hot water, the orthophosphoric acid, H_3PO_4, is formed.

$$P_4O_{10} + 6H_2O = 4H_3PO_4$$

Phosphorus pentoxide is a very effective drying agent for all gases, except those which are basic, such as ammonia. For this purpose, the pentoxide is usually shaken with dry glass beads or pieces of dry pumice, and the latter then charged into suitable U-tubes through which the gas to be dried is passed. By spreading out the pentoxide in a thin layer in this way its effective life is considerably increased, since its efficiency as a drying agent is appreciably reduced as soon as the "skin" of meta-phosphoric acid forms.

The dehydrating action of phosphorus pentoxide is also shown in its ability to remove the elements of water from many organic and inorganic compounds. Examples of this reactivity occur with—

(*a*) Concentrated sulphuric acid—

$$H_2SO_4 - H_2O = \underset{\text{trioxide}}{\overset{\text{sulphur}}{SO_3}}$$

(*b*) Concentrated nitric acid—

$$2HNO_3 - H_2O = N_2O_5$$

nitrogen pentoxide

(*c*) Glacial acetic acid—

$$\begin{matrix} CH_3 . COO \\ CH_3 . CO \end{matrix} \begin{matrix} H \\ OH \end{matrix} - H_2O = \begin{matrix} CH_3 . CO \\ CH_3 . CO \end{matrix} O$$

acetic anhydride

(*d*) Acetamide—

$$CH_3 . CONH_2 - H_2O = CH_3 . CN$$

acetonitrile

Structure of the Oxides. These are all based on the tetrahedral arrangement of the four phosphorus atoms found in the phosphorus molecule (*see* Fig. 216).

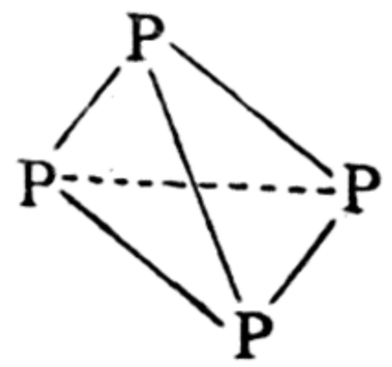


FIG. 216. Phosphorus Molecule

The phosphorous oxide, P_4O_6, has the structure shown in Fig. 217, in which each P—P linkage is replaced by a non-linear P—O—P arrangement. The P—P inter-atomic distance is greater than in the P_4 molecule, so that this linkage disappears and the phosphorus retains its trivalency.

In phosphorus pentoxide, P_4O_{10}, the four additional oxygen atoms are directly attached by double bonds to the phosphorus atoms, as shown in Fig. 218. Each phosphorus atom then shows its higher valency of five.

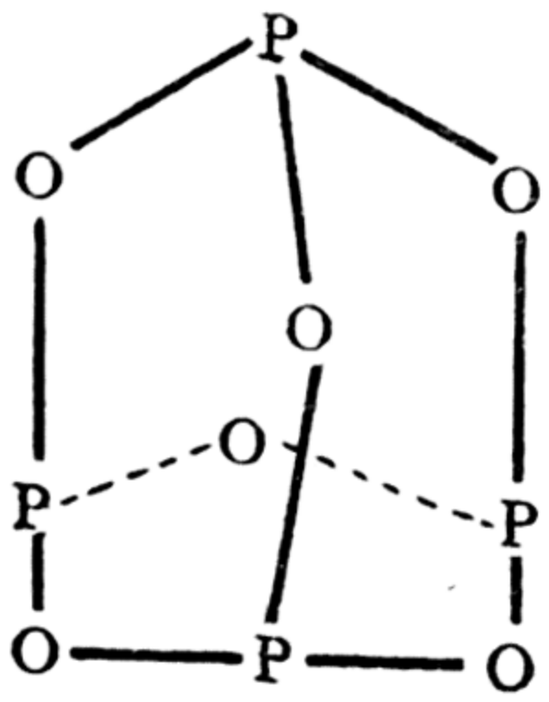


FIG. 217. Phosphorous Oxide

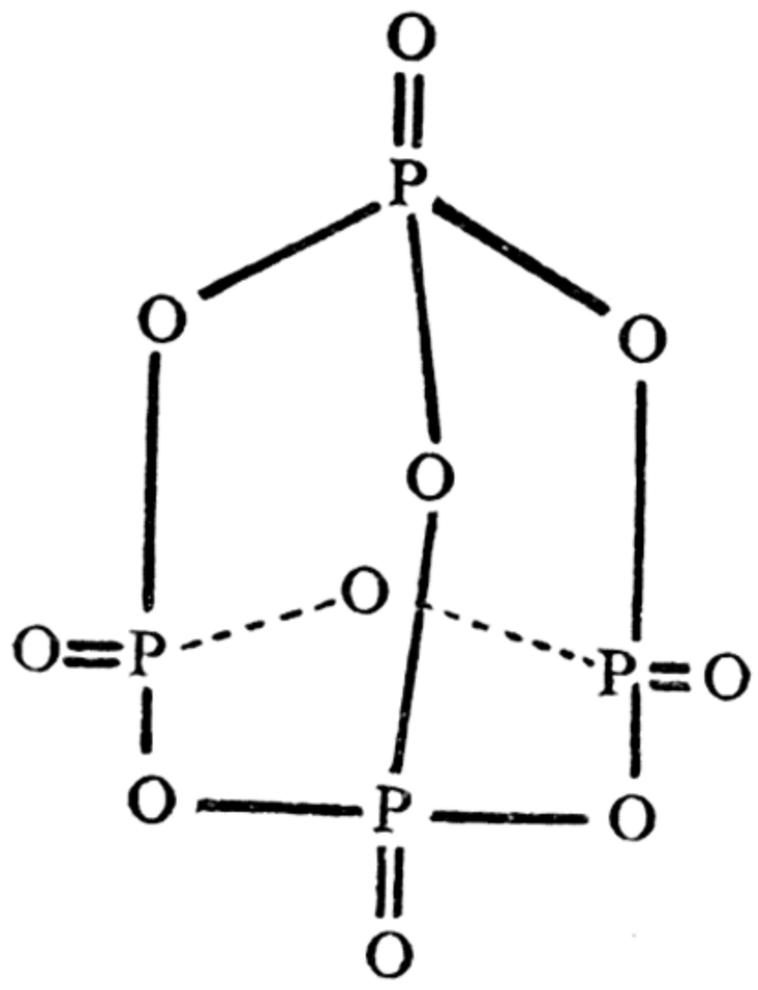


FIG. 218. Phosphorus Pentoxide

The oxide, P_4O_8, is less definite, but is almost certainly based on the same tetrahedral arrangement of the four phosphorus atoms, except that there are fewer oxygen bridges or fewer directly bonded oxygen atoms.

Hypophosphorous Acid, H_3PO_2. Salts of this acid are prepared when white phosphorus is boiled with aqueous solutions of the alkalis, as in the preparation of phosphine.

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3 \uparrow$$

The free acid may be obtained by adding dilute sulphuric acid to a solution of the barium salt, filtering off the precipitated barium sulphate and evaporating to crystallize the hypophosphorous acid.

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 \downarrow + 2H_3PO_2$$

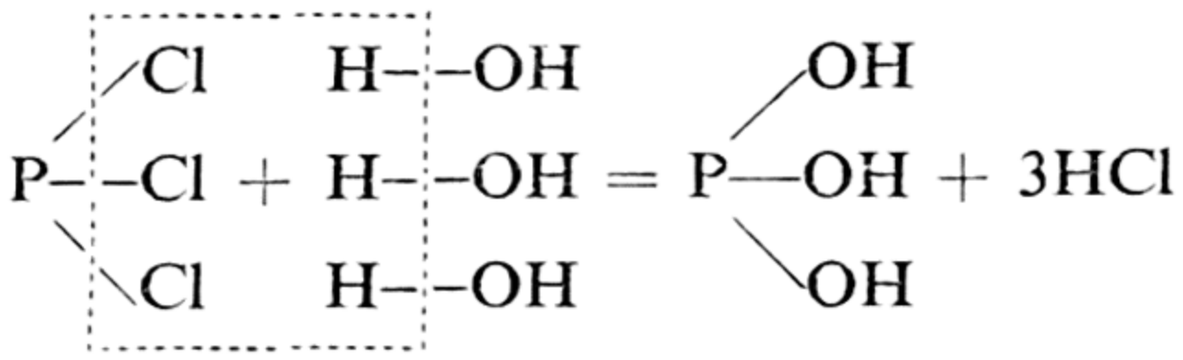
The acid is only monobasic, so that its salts are of the type NaH_2PO_2. On heating, the acid decomposes into phosphine and phosphoric acid, a reaction which is shared by all the lower acids of phosphorus—

$$2H_3PO_2 = H_3PO_4 + PH_3 \uparrow$$

The acid and its salts are very powerful reducing agents, and precipitate many metals from their salts; with copper sulphate, the red precipitate is thought to be copper hydride, Cu_2H_2, and this reaction is often used in the detection of hypophosphites.

Phosphorous Acid, H_3PO_3. This acid may be prepared by dissolving the trioxide in cold water, or more conveniently by the action of water on phosphorus trichloride, PCl_3. The latter method recalls the laboratory method for making hydrogen bromide and hydrogen iodide—*see* p. 797.

$$P_4O_6 + 6H_2O = 4H_3PO_3$$



The solid acid, m. p. 70°C, may be obtained by evaporating the solution until the temperature rises to 180°C, and then cooling.

It is a weak acid, and is thought to be dibasic from the fact that most of its salts, the phosphites, are of the form Na_2HPO_3.

A self oxidation-reduction reaction occurs on heating to form phosphine and ortho-phosphoric acid—

$$4H_3PO_3 = 3H_3PO_4 + PH_3 \uparrow$$

The tendency to change to orthophosphoric acid is also shown by its slow oxidation to this acid by the oxygen of the air, and by its powerful reducing properties. Thus, it precipitates copper, silver and gold from solutions of their salts, and reduces mercuric chloride to mercurous chloride or to mercury—

$$2HgCl_2 + H_3PO_3 + H_2O = Hg_2Cl_2 + H_3PO_4 + 2HCl$$

The phosphites are soluble in water and, like the acid, are powerful reducing agents.

Hypophosphoric Acid, $H_4P_2O_6$. This acid is formed, together with other phosphorous and phosphoric acids, when white phosphorus is exposed to a limited supply of moist air. The acid has been isolated and shown to be stable at ordinary temperatures, but it is hydrolyzed by the mineral acids to form a mixture of phosphoric and phosphorous acids

$$H_4P_2O_6 + H_2O = H_3PO_4 + H_3PO_3$$

The Phosphoric Acids

These acids and more particularly their salts are very important.

Three well-defined phosphoric acids are known, and these may be regarded as derived from the parent oxide, phosphorus pentoxide, by combination with various amounts of water—

$$P_4O_{10} + 2H_2O = 4HPO_3$$

metaphosphoric acid

$$P_4O_{10} + 4H_2O = 2H_4P_2O_7$$

pyrophosphoric acid

$$P_4O_{10} + 6H_2O = 4H_3PO_4$$

orthophosphoric acid

The true ortho-acid, $P(OH)_5$ or H_5PO_5, is not known; the description "ortho-" is therefore applied to the next acid, H_3PO_4.

Orthophosphoric Acid, H_3PO_4. This acid is prepared by burning white phosphorus in excess of air or oxygen and dissolving the resulting phosphorus pentoxide in hot water.

$$P_4O_{10} + 6H_2O = 4H_3PO_4$$

The process is carried out commercially—

(*a*) By admitting air to the phosphorus vapour as it distils over from the electric furnace and then dissolving out the phosphorus pentoxide in a tower down which passes a spray of water.

(*b*) By burning the white phosphorus in a separate plant and dissolving out the phosphorus pentoxide as in (*a*).

(*c*) By heating white phosphorus with water under pressure at 600°–700°C in presence of a catalyst such as nickel.

Phosphoric acid is also manufactured from calcium phosphate by treatment with sulphuric acid, as described in the first part of the now obsolete wet-process for phosphorus (*see* p. 669)—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4\downarrow + 2H_3PO_4$$

A convenient laboratory method for making orthophosphoric acid is to boil red phosphorus with slightly diluted nitric acid (sp. gr. 1·20–1·25). The reaction is best carried out in a flask provided with a reflux condenser, and a trace of iodine added. Copious brown fumes of nitrogen peroxide are evolved, and when these cease, the temperature is slowly raised to about 180°C to concentrate the solution.

$$P + 5HNO_3 = H_3PO_4 + 5NO_2\uparrow + H_2O$$

Properties of Orthophosphoric Acid. Anhydrous orthophosphoric acid is a white solid, m. p. 42·3°C. It is available commercially as the concentrated solution which is a colourless syrupy liquid. When heated to about 250°C for some time, it is partially dehydrated to form pyrophosphoric acid, and at still higher temperatures, (about 600°C), further decomposition occurs to form metaphosphoric acid—

$$2H_3PO_4 = H_4P_2O_7 + H_2O$$

$$H_4P_2O_7 = 2HPO_3 + H_2O$$

Orthophosphoric acid is tribasic, and forms normal and acid phosphates, such as—

Na_3PO_4 = normal or trisodium phosphate

Na_2HPO_4 = disodium hydrogen phosphate

NaH_2PO_4 = sodium dihydrogen phosphate

These salts may most easily be prepared by adding the appropriate amount of alkali to the orthophosphoric acid. Since the concentration of the latter solution is, however, uncertain, it may not be possible to calculate the respective amounts of alkali required, and it becomes necessary to follow a titration method based on a knowledge of the acid or alkaline behaviour of the different sodium phosphates in solution.

Salt	Behaviour in Solution	Indicator
NaH_2PO_4 .	Neutral to methyl orange but acid to phenolphthalein	Methyl Orange
Na_2HPO_4 .	Neutral to phenolphthalein but alkaline to methyl orange	Phenolphthalein (or, better, thymolphthalein)
Na_3PO_4 .	Alkaline to all indicators because of its extended hydrolysis	None suitable

The procedure may be illustrated for the case in which phenolphthalein indicator is used. 25 ml of the orthophosphoric acid solution are titrated against a solution of sodium hydroxide. At the point of neutrality to the phenolphthalein indicator, the reaction which has occured is—

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$$

and the solution contains only the disodium salt, Na_2HPO_4. If V ml of the sodium hydroxide solution have been added at this point, then consideration of the following equations shows how solutions of the other sodium phosphates may be obtained—

$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$$
$$H_3PO_4 + \ NaOH = NaH_2PO_4 + H_2O$$

Using fresh portions of the *same* solutions as were previously used, then—

$$25 \text{ ml } H_3PO_4 + 3V/2 \text{ ml NaOH} \rightarrow \text{solution of } Na_3PO_4$$
$$25 \text{ ml } H_3PO_4 + V \text{ ml NaOH} \rightarrow \text{solution of } Na_2HPO_4$$
$$25 \text{ ml } H_3PO_4 + V/2 \text{ ml NaOH} \rightarrow \text{solution of } NaH_2PO_4$$

Trisodium phosphate, however, is only stable in the solid state, and may be obtained by evaporating the above solution to dryness. In water the following hydrolysis occurs, so that the solution is alkaline—

$$Na_3PO_4 + H_2O = Na_2HPO_4 + NaOH$$

The *sodium phosphate* used as a laboratory reagent is the disodium compound, $Na_2HPO_4 . 12H_2O$. *Microcosmic salt* is a mixed phosphate having the composition $NaNH_4HPO_4 . 4H_2O$. Another well known mixed phosphate is the precipitate of $Mg(NH_4)PO_4$ formed on adding sodium phosphate to an ammoniacal solution of a magnesium salt.

The heavy metals usually only form the *insoluble* normal phosphates, such as, Ag_3PO_4, which is precipitated on adding any of the orthophosphates to a solution of a silver salt—

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 \downarrow + 2NaNO_3 + HNO_3$$

Action of Heat on Orthophosphates. Only the normal (or tertiary) orthophosphates are unchanged on heating. The primary and secondary orthophosphates all lose water and form the pyrophosphates or metaphosphates as indicated in the following equations—

$$2Na_2HPO_4 - H_2O = \underset{\text{sodium pyrophosphate}}{Na_4P_2O_7}$$

$$NaH_2PO_4 - H_2O = \underset{\text{sodium metaphosphate}}{NaPO_3}$$

$$2Mg(NH_4)PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$$
$$Na(NH_4)HPO_4 = NaPO_3 + NH_3 + H_2O$$

Superphosphate is a mixture of calcium dihydrogen phosphate and

calcium sulphate, and is prepared by heating powdered mineral phosphate with Chamber sulphuric acid at about 100°C for periods up to a day—

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$$

The resulting acid phosphate is more soluble than the normal calcium phosphate and is therefore more easily assimilated by plants. Its importance as a fertilizer is reflected in the statement that more than a half of the total world production of phosphorus compounds is in this form. It should also be noted that the manufacture of superphosphate consumes the greater portion of the sulphuric acid produced by the Chamber process.

Pyrophosphoric Acid, $H_4P_2O_7$. When orthophosphoric acid is heated for some time at about 250°C it loses water to form pyrophosphoric acid.

$$2H_3PO_4 = H_4P_2O_7 + H_2O$$

The reaction is reversible, occurring slowly with cold water but more rapidly on boiling. It is a colourless solid, of low melting point, and is tetrabasic, although so far only the normal and dihydrogen pyrophosphates have been prepared, $Na_4P_2O_7$ and $Na_2H_2P_2O_7$. The former of these is prepared, as described above, by heating the monohydrogen orthophosphate.

Metaphosphoric Acid, HPO_3. When phosphorus pentoxide is used as a drying agent at ordinary temperatures, it quickly hydrates to form a film of the deliquescent meta-phosphoric acid. Further hydration to form the orthophosphoric acid then occurs very much more slowly. Metaphosphoric acid may also be prepared from the latter acid by heating to about 600°C—

$$H_3PO_4 = HPO_3 + H_2O$$

It is a water-white deliquescent glassy solid, and is sometimes called *glacial phosphoric acid.* It combines with water, slowly in the cold, but more rapidly on boiling, to form orthophosphoric acid.

The vapour density at very high temperatures corresponds to $(HPO_3)_2$, but it is probable that the molecular formula at ordinary temperatures is $(HPO_3)_n$, where n indicates a higher degree of polymerization. This view is supported by the formation of such metaphosphates as sodium hexametaphosphate, $(NaPO_3)_6$, and sodium trimetaphosphate, $(NaPO_3)_3$. These metaphosphates are prepared by strongly heating the monosodium orthophosphate, NaH_2PO_4, the disodium dihydrogen pyrophosphate, $Na_2H_2P_2O_7$, or microcosmic salt, $Na(NH_4)HPO_4$, until the mass fuses. On rapid cooling of the melt, sodium hexametaphosphate is obtained as a transparent vitreous mass. If the cooling is not rapid, sodium tri-metaphosphate is formed.

Sodium Hexametaphosphate. Considerable quantities of this compound are now manufactured for the softening of hard water for washing purposes and in the treatment of water used in boilers. Its use for these purposes is

based on its remarkable property of dissolving even the most insoluble calcium compounds, so that it not only prevents the precipitation of calcium salts and the formation of scale, but also may dissolve existing deposits of calcium sulphate and carbonate previously formed in boilers, condenser tubes, etc. This solvating action is thought to be due to the formation of soluble complex salts, in which calcium enters the anion—

$$Na_2[Na_4(PO_3)_6] + 2CaSO_4 = Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4$$

Similar reactions probably occur with other metallic salts; thus addition of sodium hexametaphosphate to a solution of a ferric salt inhibits the formation of the characteristic red colour on adding a thiocyanate solution.

Calgon is a commercial form of sodium hexametaphosphate which contains about ten per cent of tetrasodium pyrophosphate, $Na_4P_2O_7$.

Phosphate Beads. When a little microcosmic salt is heated on a platinum wire in a bunsen flame, it forms a colourless glass bead. When small quantities of oxides of certain metals are placed on the bead, and the heating repeated, a coloured bead may be obtained, the colour being indicative of the metal. Thus cobalt oxide produces a blue bead, due to the formation of the orthophosphate $NaCoPO_4$—

$$NaPO_3 + CoO = NaCoPO_4$$

Reactions for Identifying Phosphates. Since all the phosphoric acids produce the phosphate ion, $(PO_4)^{---}$, in water, the following test for this ion may be used in the first place to identify the presence of a phosphate. If a yellow precipitate (a complex ammonium phosphomolybdate) forms on gently warming the solution obtained on adding nitric acid and excess of ammonium molybdate, the presence of a phosphate is indicated. The temperature should not exceed 40°C if the presence of an arsenate is also suspected, since the latter forms a similar yellow precipitate at higher temperatures.

The following reactions may then be used to identify the particular phosphate present—

Reagent	Orthophosphate	Pyrophosphate	Metaphosphate
Silver nitrate . .	Yellow ppt.	White cryst. ppt.	White gel. ppt.
Albumen . . .	Nil	Nil	Coagulated
Zinc acetate . .	Nil	White ppt.	Nil

The determination of phosphates may be carried out gravimetrically or volumetrically.

Gravimetrically. The precipitate of magnesium ammonium phosphate,

obtained on adding magnesium sulphate (or chloride) and ammonium chloride to an ammoniacal solution of the phosphate, is collected in a weighed Gooch or sinter crucible. The latter is then heated to redness to convert the magnesium ammonium phosphate to magnesium pyrophosphate and, after cooling in a desiccator, is reweighed.

$$2Mg(NH_4)PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$$

Volumetrically. Phosphates may also be determined volumetrically by titration with uranyl nitrate (or acetate) in presence of ammonium acetate, using potassium ferrocyanide as external indicator; or by precipitating ammonium phosphomolybdate which is then dissolved in excess standard sodium hydroxide and back titrated with standard nitric acid solution.

Compound	Uses
H_3PO_4	In soft drinks, table-jellies, etc., to impart tartness; catalytic conversion of ethyl alcohol to ethylene; etching of metal surfaces prior to painting or lacquering; with oxidizing agents in rust-proofing and anticorrosive treatment of metals.
$CaH_4(PO_4)_2$	Impure as *superphosphate* fertilizer; the pure compound is used in baking powders—it improves the ageing properties of bread and prevents the outbreak of the disease known as "ropiness."
$Na_2H_2P_2O_7$	In baking powders and self-raising flours. It reacts only slowly with sodium bicarbonate in the cold, but rapidly at oven temperatures. $CaHPO_4$ is often added.
Na_3PO_4	In treatment of textiles and in water softening. It is a constituent of many proprietary soap powders, due to its alkalinity in solution and to its emulsifying action. It is used alone or with soda-ash, sodium metasilicate, borax, or soap.
$(NaPO_3)_6$	In water treatment for washing and boiler purposes, due to its ability to retain calcium and magnesium salts in solution.
P_2O_5	Used in laboratories for drying gases and liquids, and occasionally in organic synthesis as a dehydrating agent.
Medicinal phosphates	These include glycerophosphates, hypophosphites, as well as sodium and calcium phosphates.
Phosphoric esters	Organic esters, such as tricresyl-, tributyl-, and tri-phenyl phosphates are liquids of high boiling points and very low volatility. They are used as plasticizers in the plastic and lacquer industries.
Sodium and ammonium phosphates	Used extensively in the treatment of wood and textiles for flame-proofing purposes.

Industrial Uses of the More Important Phosphorus Compounds. The Table on p. 688 gives a summary of the more important phosphorus compounds together with some of their principal uses.

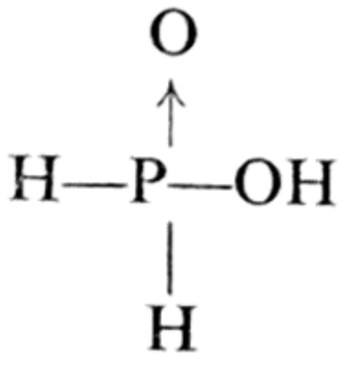
Structural Formulae of the Phosphorus Acids. In determining the structure of the phosphoric acids, consideration has to be given to the following points—

(*a*) A hydrogen directly attached to phosphorus appears not to be acidic; thus phosphine, PH_3, is very slightly alkaline, but not acidic.

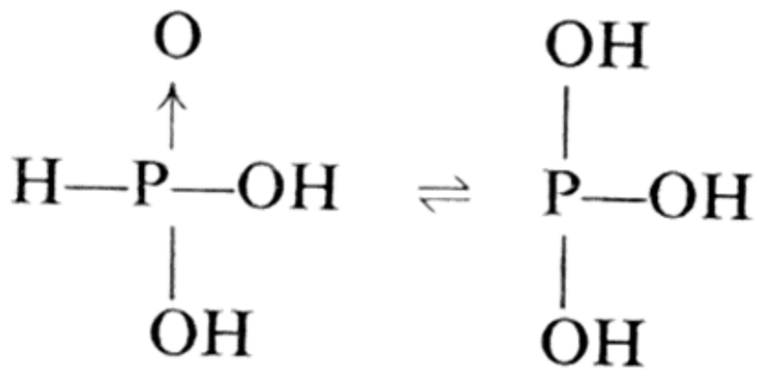
(*b*) The acidic hydrogen atoms appear to be linked to the phosphorus atom through an oxygen atom, P—O—H.

(*c*) The basicity is not always equal numerically to the number of hydrogen atoms in the molecule; H_3PO_2 is monobasic; H_3PO_3 is mainly dibasic; H_3PO_4 is tribasic.

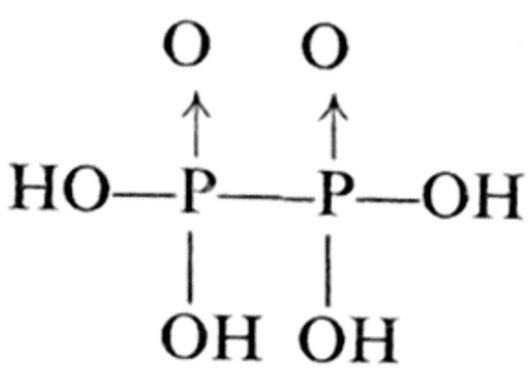
Consideration of these facts suggests the following structural formulae—



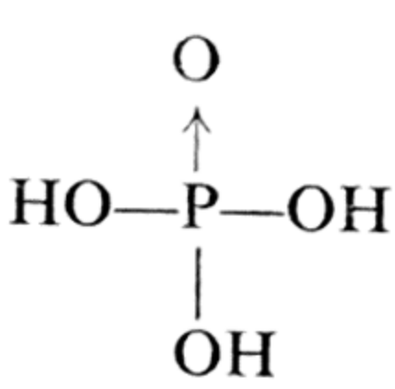
Hypophosphorous acid, H_3PO_2



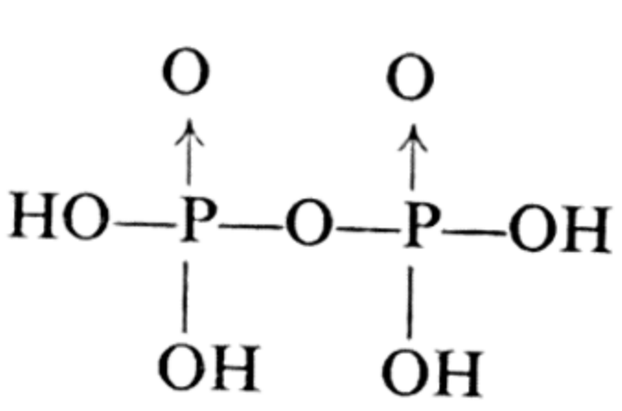
Phosphorous acid, H_3PO_3



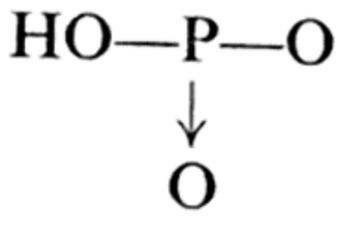
Hypophosphoric acid, $H_4P_2O_6$



Orthophosphoric acid, H_3PO_4



Pyrophosphoric acid, $H_4P_2O_7$



Metaphosphoric acid, HPO_3

or possibly the alternative structures in which the co-ordinate links, P→O are each replaced by a true double bond, P=O.

Other Compounds of Phosphorus

Fluorides	*Chlorides*	*Bromides*	*Iodides*
PF_3 gas b. p. − 95°C	PCl_3 liquid b. p. 74°C	PBr_3 liquid b. p. 174°C	PI_3 solid m. p. 41°C
PF_5 gas b. p. − 75°C	PCl_5 solid sublimes	PBr_5 solid sublimes	P_2I_4 solid

Phosphorus Trichloride, PCl_3, forms when phosphorus burns in chlorine. The reaction is carried out by passing a current of dry chlorine over white phosphorus in the complete absence of moisture. The phosphorus is gently warmed to initiate the reaction and the phosphorus trichloride collected in the receiver. If the chlorine delivery tube is too far above the phosphorus, the pentachloride is the main product, whilst if it is too near, the heat of the reaction leads to some distillation of the phosphorus.

Phosphorus trichloride is a colourless liquid, boiling point 74°C. It

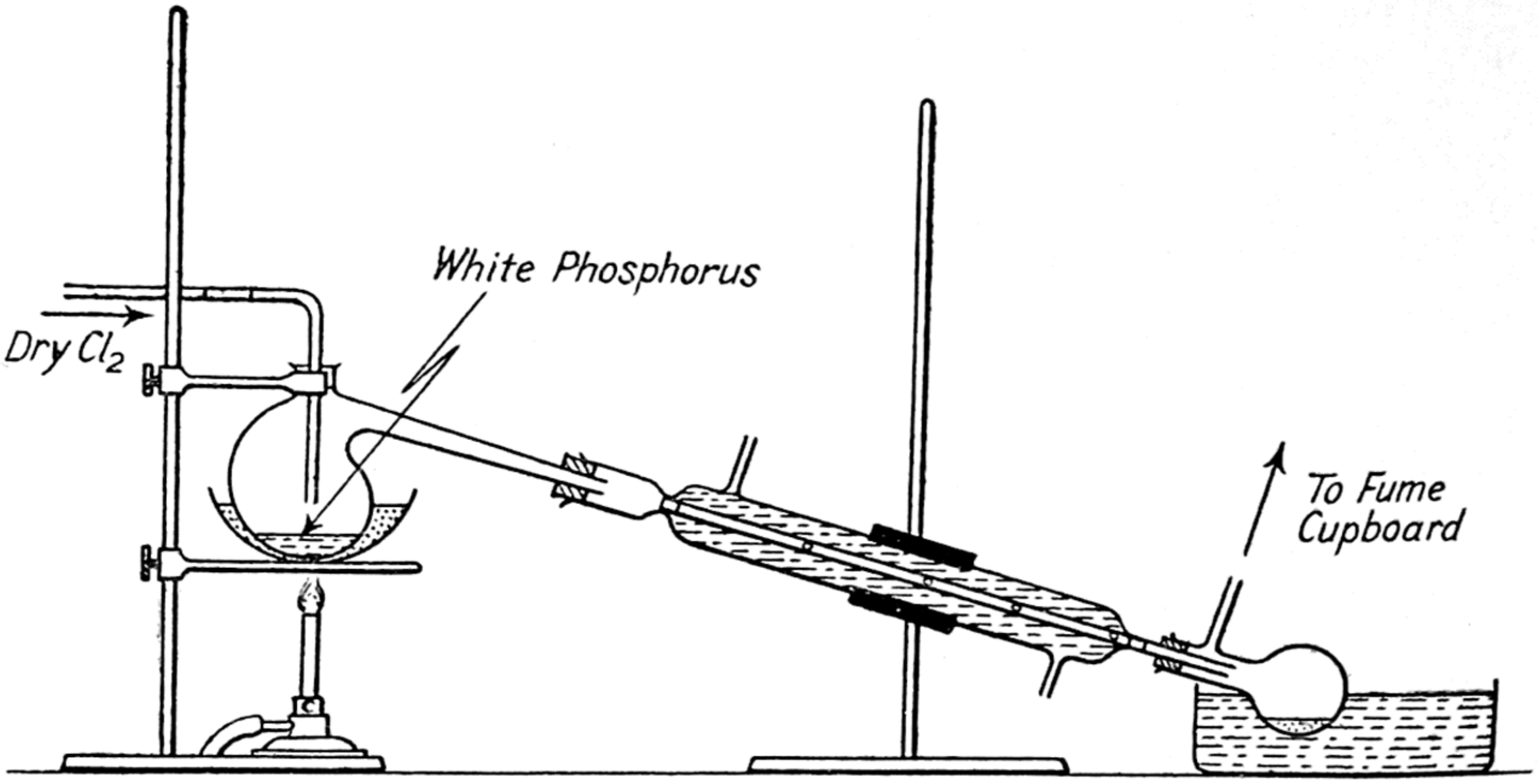


FIG. 219. Preparation of Phosphorus Trichloride

fumes in moist air due to the formation of hydrogen chloride, the hydrolysis occurring completely with water—

$$\begin{matrix} & Cl & H- & -OH \\ P- & -Cl & + H- & -OH \\ & Cl & H- & -OH \end{matrix} = H_3PO_3 + 3HCl$$

Phosphorus Pentachloride, PCl_5, is formed when phosphorus burns in excess of chlorine. It is conveniently prepared by the action of excess of dry chlorine on the liquid trichloride. The reaction is carried out in the apparatus as shown; phosphorus trichloride is admitted drop-wise from the funnel into a bottle through which passes a current of dry chlorine gas.

$$PCl_3 + Cl_2 = PCl_5$$

Phosphorus pentachloride is a pale greenish-yellow solid, which dissociates below 100°C when heated. If heated under pressure, however, it melts at

140°–150°C. The dissociation, on heating at normal pressures, into phosphorous chloride and chlorine is reversible, the percentage dissociation increasing with increase in temperature—

$$PCl_5 = PCl_3 + Cl_2$$

The percentage dissociation at any particular elevated temperature may be obtained from a determination of the vapour density, as described on p. 31. In accordance with the law of mass action, the dissociation will be repressed in an atmosphere of chlorine gas.

Phosphorus pentachloride fumes in moist air, and reacts violently with water. If the amount of water is limited, the liquid phosphorus oxy-chloride is formed, but with excess water the product is orthophosphoric acid—

$$PCl_5 + H_2O = POCl_3 + 2HCl$$
$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl$$

Phosphorus Oxychloride, $POCl_3$, is prepared by carefully adding water to the pentachloride until the solid disappears. It is a colourless fuming liquid, b. p. 107°C, and distils over at this temperature without decomposition.

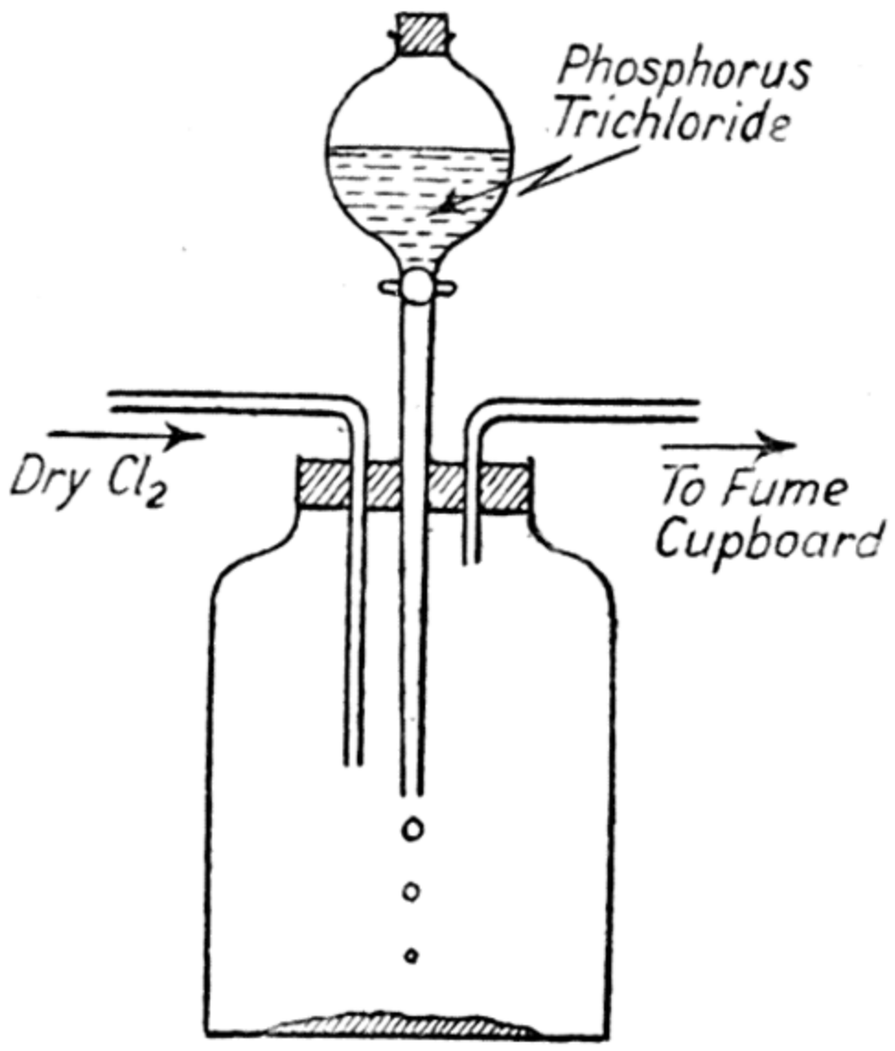


FIG. 220. Preparation of Phosphorus Pentachloride

Phosphorus Bromides and Iodides are prepared similarly by direct combination of the halogen with white phosphorus. Their properties resemble those of the corresponding chlorides, and they are all more or less rapidly hydrolyzed by water. The preparation of hydrogen bromide and hydrogen iodide by hydrolysis of the corresponding phosphorus trihalides has already been described (*see* p. 682).

Phosphorus Fluorides cannot be prepared by direct combination because of the difficulties associated with the preparation and handling of free fluorine. They may however be prepared by reactions such as—

$$3PbF_2 + Cu_3P_2 = 3Pb + 3Cu + 2PF_3$$
$$AsF_3 + PCl_3 = AsCl_3 + PF_3$$
$$5AsF_3 + 3PCl_5 = 5AsCl_3 + 3PF_5$$

Phosphorus Pentafluoride is interesting principally because of its very great stability. Unlike the pentachloride, it does not dissociate on heating, and has a normal covalent structure with the phosphorus atom at the centre of a regular trigonal bipyramid. The pentachloride however has a structure based on a packing of PCl_4^+ and PCl_6^- ions (*see* Fig. 221).

TABLE 99

Comparison of Nitrogen, Phosphorus and Sulphur, and of their Components

Nitrogen	Phosphorus	Sulphur
Relatively inert colourless gas	Reactive coloured solid, low melting point	Less reactive coloured solid, low melting point
Slightly soluble in water	Soluble in CS_2 and insoluble in water	Soluble in CS_2 and insoluble in water
Does not burn in air or oxygen	Burns in air and oxygen $\rightarrow P_4O_6$ and P_4O_{10}	Burns in air and oxygen $\rightarrow SO_2$ and SO_3
No allotropes	Forms allotropes (W.P., R.P. etc.)	Forms allotropes (α and β S, etc.)
Does not combine directly with chlorine	Burns in chlorine $\rightarrow PCl_3$ and PCl_5	Burns in chlorine $\rightarrow S_2Cl_2$, SCl_2, and SCl_4
No reaction with cold or hot NaOH	W.P. soluble in hot NaOH $\rightarrow PH_3$	Soluble in hot NaOH
NH_3, basic, burns only in oxygen, very soluble in water, not poisonous	PH_3, feebly basic, very inflammable, insoluble in water, very poisonous	H_2S, feebly acidic, burns in air, soluble in water, very poisonous
Oxides are all endothermic, and therefore *unstable*	Oxides are all exothermic, and therefore *stable*	Oxides are exothermic (SO_2 and SO_3) and are therefore *stable*
N_2O_3, N_2O_4, N_2O_5 unstable acid anhydrides	P_4O_6, P_4O_8, P_4O_{10} stable acid anhydrides	SO_2, SO_3 stable acid anhydrides
Highest acid most stable (HNO_3, cf. HNO_2)	Highest oxide and acid most stable (H_3PO_4, cf. H_3PO_3)	Highest acid most stable (H_2SO_4, cf. H_2SO_3)
Only one nitric acid	Several phosphoric acids (pyro-, meta-, ortho-)	Several sulphuric acids (pyro-, normal-)
HNO_3 some oxidizing and some reducing properties	H_3PO_2 and H_3PO_3 are reducing agents	$H_2S_2O_4$ and H_2SO_3 are reducing agents
N_2O_5 dissolves in water to give HNO_3	P_4O_{10} enormous affinity for water $\rightarrow HPO_3$ and H_3PO_4, both weak acids	SO_3 considerable affinity for water $\rightarrow H_2SO_4$ and $H_2S_2O_7$, both strong acids
HNO_3—a strong acid		
NH_4Cl with NaOH $\rightarrow NH_3$	PH_4Cl with NaOH $\rightarrow PH_3$	—
N_2 combines directly with some metals $\rightarrow$ nitrides, e.g. Mg_3N_2	P_4 combines directly with most metals $\rightarrow$ phosphides, e.g. Ca_3P_2	S_8 combines directly with most metals $\rightarrow$ sulphides, e.g. CuS
Ca_3N_2 with water $\rightarrow NH_3$	Ca_3P_2 with water $\rightarrow PH_3$	CaS with water $\rightarrow H_2S$
N_2H_4 neutral liquid	P_2H_4 spontaneously inflammable liquid	—
NCl_3 *explosive* and $\rightarrow NH_3$ on hydrolysis	PCl_3 stable and $\rightarrow H_3PO_3$ and HCl on hydrolysis	S_2Cl_2 stable and $\rightarrow H_2SO_3$, HCl and S on hydrolysis
NCl_5 not known	PCl_5 stable, hydrolyzed by water	SCl_2 and SCl_4 hydrolyzed by water
NF_3 insoluble and unattacked by water or alkalis	PF_3 hydrolyzed by water or alkalis	SF_4 hydrolyzed by water or alkalis
NF_5 not known	PF_5 *very stable*, not attacked by water or alkalis	SF_6 *very stable*, not attacked by water or alkalis
All nitrates soluble	Most phosphates are insoluble	Ca, Sr, Ba sulphates insoluble

Phosphorus Sulphides. White phosphorus unites explosively with sulphur on heating, but the reaction may be controlled if red phosphorus be used instead of the white phosphorus. With correct proportions, *phosphorus pentasulphide*, P_2S_5, may be obtained. The latter may then be purified by distillation from a retort through which passes a stream of an inert gas, such as carbon dioxide. It is a yellow solid, m. p. 290°C, b. p. 515°, and like the halides is hydrolyzed by water—

$$P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S\uparrow$$

Other sulphides, such as P_4S_3 (used in making matches) and P_4S_7 may be prepared by heating red phosphorus and sulphur together in the correct proportions as indicated by their formulae.

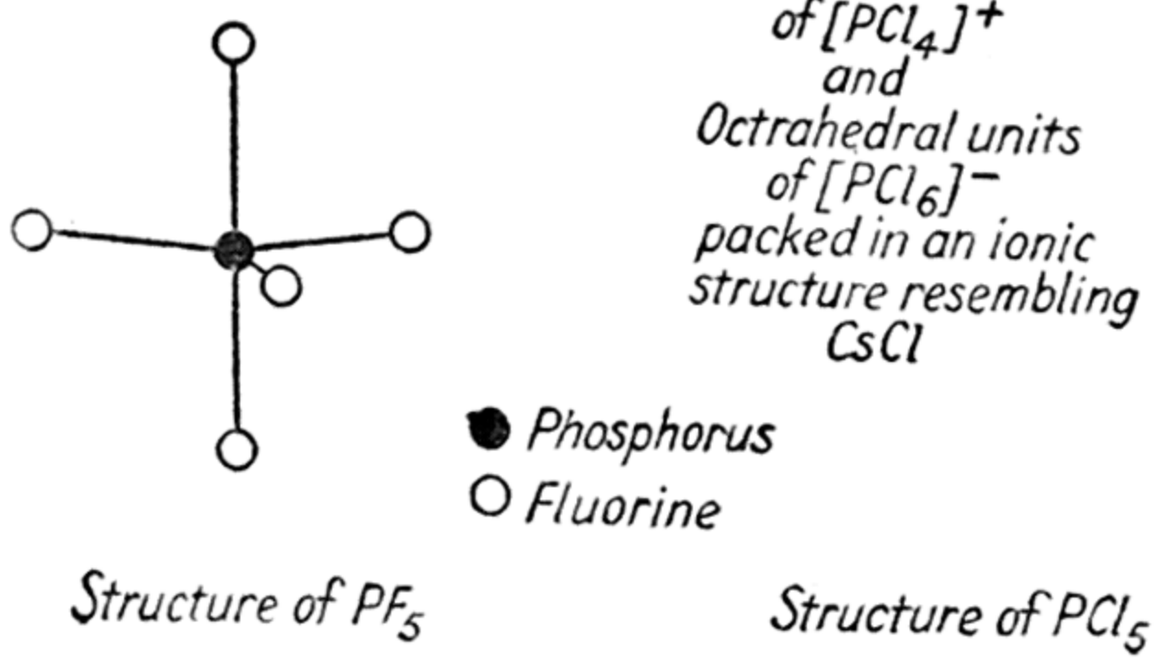


FIG. 221. Structure of Phosphorus Pentafluoride and Phosphorus Pentachloride

Phosphorus Compared with Nitrogen and with Sulphur

Although phosphorus follows nitrogen in the Group V family of elements, its properties are in many respects very different from those of nitrogen and are more closely related to those of sulphur, the adjoining Group VI element. The difference in properties between nitrogen and phosphorus recalls that many of the properties of fluorine are also different from those of its next family element, namely chlorine. In the following table an attempt is made to compare and contrast the properties of nitrogen, phosphorus and sulphur, so as to reveal these differences and similarities, but at the outset is should be stated that the different valencies of phosphorus, 3 and 5, and sulphur 2, 4 and 6, must produce a difference in formulae of compounds which may otherwise be similar in their properties.

ARSENIC, ANTIMONY, BISMUTH

The B sub-group elements, arsenic, antimony and bismuth, show a much closer resemblance to nitrogen and to phosphorus than do the A sub-group elements, vanadium, niobium and tantulum, and they are therefore appropriately discussed at this stage after phosphorus. The discussion of

the A sub-group elements, which are comparatively rare, is left to the more comprehensive textbook.

Occurrence. The principal naturally occurring minerals containing these elements are the sulphides and to a lesser extent the oxides. The elements also occur in the free, or native states, although only in the case of bismuth are the deposits sufficiently concentrated to be an important source of the element. The most important minerals are—

(*a*) Of arsenic: *Realgar*, As_2S_2; *Orpiment*, As_2S_3; *Mispickel* or *Arsenical Pyrites*, FeAsS; and *Arsenolite*, As_4O_6. Arsenic also occurs in most pyrites and in zinc blende.

(*b*) Of antimony: *Stibnite*, Sb_2S_3 (a black mineral with a metallic lustre); of less importance are the various oxides, such as Sb_2O_3 (antimony bloom) and Sb_2O_4 (antimony ochre).

(*c*) Of bismuth; *Bismuthite*, a basic bismuth carbonate; Bismuth glance, Bi_2S_3, is comparatively rare. Native deposits are the most important.

Arsenic is obtained either as a natural product or by strongly heating arsenical pyrites, when the arsenic sublimes over and is collected—

$$FeAsS = FeS + As \text{ (sublimes)} \uparrow$$

Considerable quantities of arsenic are recovered from the oxide sublimate which collects in the flues on roasting many other sulphides ores, such as pyrites and zinc blende. The oxide is reduced to the element by mixing with powdered carbon and heating in a clay crucible, provided with a conical iron-cap to collect the arsenic sublimate—

$$As_4O_6 + 6C = 6CO \uparrow + 4As \uparrow$$

Antimony is obtained commercially by heating stibnite, Sb_2S_3, with scrap iron—

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS$$

The ferrous sulphide collects as a molten slag over the molten antimony, and so may easily be separated. The antimony is then purified from the easily oxidizable impurities, such as sulphur, arsenic and lead, by remelting several times with small quantities of sodium nitrate. Antimony is also obtained from poorer sulphide ores by the following sequence of operations—

(*a*) concentration of the sulphide ores by *liquation*,

(*b*) roasting the concentrated ore in air to form the oxide, Sb_2O_3, and

(*c*) reducing the oxide by heating with carbon (the sulphide cannot be reduced directly)—

$$Sb_2O_3 + 3C = 2Sb + 3CO$$

Bismuth is obtained similarly from sulphide ores. After concentration of

the ores by flotation methods, it is first roasted to the oxide, and the latter then reduced to the metal by heating with carbon in a reverberatory furnace (*see* p. 456).

$$2Bi_2S_3 + 9O_2 = 2Bi_2O_3 + 6SO_2$$
$$Bi_2O_3 + 3C = 2Bi + 3CO$$

Bismuth is also obtained from the native deposits simply by heating and allowing the molten bismuth to run away from the less fusible solid impurities, that is, by liquation.

Physical Properties. Arsenic, antimony and bismuth are all semi-metals, the metallic character increasing from arsenic to bismuth, and for this reason they are often referred to as *metalloids*. In one or other of their allotropic forms, they show a typically metallic lustre and conduct heat and electricity. They are however too brittle to be used by themselves as metals, but they form several important alloys with other metals (*see* "Uses").

TABLE 100

Properties of Arsenic, Antimony and Bismuth

Property	Arsenic	Antimony	Bismuth
Density . . .	4·69–5·72	6·63	9·78
Melting point . .	Sublimes at ordinary pressures	630°C	271°C
Boiling point . .		1380°C	1450°C
Molecule (vapour) .	As_4	Sb_4	Bi_2
Stable form appearance	Grey metallic lustre	White metallic lustre	White metallic lustre
Electrical conductivity	4 per cent of Cu	4 per cent of Cu	1 per cent of Cu
Heat conductivity .	Fairly good	Poor; Expands on solidification	Bad; Expands on solidification
Other allotropic forms.	Yellow-As	Yellow-Sb	—
	Black-As	Black-Sb	—

Allotropy

Arsenic

(*a*) α-Arsenic or yellow arsenic is obtained on rapidly condensing arsenic vapour. It resembles white phosphorus in its solubility in carbon disulphide, in its relative instability and high reactivity.

(*b*) β-Arsenic or black arsenic is obtained as a black crystalline deposit on heating grey arsenic in a current of hydrogen. It is insoluble in carbon disulphide, and at 360°C changes back to the grey form.

(*c*) γ-Arsenic or grey arsenic (*metallic-arsenic*) is the stable form, and is steel-grey and metallic in appearance. Its density is 5·73, and it is insoluble in carbon disulphide.

Antimony

(*a*) α-Antimony or yellow antimony is produced by the active ozonized oxygen on liquid stibine, SbH_3, at $-90°C$. It is amorphous, slightly soluble in carbon disulphide, and changes above $-90°C$ to black antimony.

(*b*) Black Antimony or explosive antimony. This is an amorphous black powder which is oxidized spontaneously in air, and on warming changes to the stable metallic antimony.

(*c*) β-Antimony or *metallic antimony* is the stable form. It is a silver-white crystalline solid with a metallic lustre, and is brittle and easily powdered.

Bismuth is a reddish-white crystalline metal, density 9·80, and like metallic antimony is brittle and easily powdered. No other forms are known.

Chemical Properties. Grey arsenic shows distinct phosphorescence when heated in air to about 200°C; at 400°C it burns to form the trioxide, As_4O_6 (but *not* the pentoxide). Antimony and bismuth also burn when heated strongly in air or in oxygen, the products again being trioxides, although in the case of antimony, smaller amounts of the tetroxide, Sb_4O_8, are also formed.

Powdered arsenic and antimony both burn spontaneously in chlorine to form the trichlorides, $AsCl_3$ and $SbCl_3$ (and some $SbCl_5$ but *not* $AsCl_5$); bismuth reacts more slowly on passing chlorine over the heated metal to form bismuth chloride, $BiCl_3$.

Arsenic, antimony and bismuth are unattacked by cold dilute acids, except in the presence of oxygen when a slow reaction occurs, probably due to intermediate formation of the trioxides by atmospheric oxidation.

Reaction occurs more readily however with the oxidizing acids, such as nitric acid and hot concentrated sulphuric acid. Thus arsenic slowly oxidizes in hot dilute nitric acid to form the trioxide, but with the concentrated acid or with aqua-regia, the product is arsenic acid—

$$As + 5HNO_3 = H_3AsO_4 + H_2O + 5NO_2$$

$$4H_3AsO_4 \xrightarrow{c.\ 200°C} As_4O_{10} + 6H_2O$$

With antimony, concentrated nitric acid forms a hydrated pentoxide, and aqua regia dissolves the antimony to give a solution of the pentachloride, $SbCl_5$. Bismuth dissolves in hot dilute nitric acid to form bismuth nitrate, $Bi(NO_3)_3$, and in aqua regia to form bismuth chloride, $BiCl_3$. Hot concentrated sulphuric acid attacks all three elements to form As_2O_3, $Sb_2(SO_4)_3$ and $Bi_2(SO_4)_3$, although an unstable sulphate is probably first formed in the case of arsenic.

Compounds of Arsenic, Antimony and Bismuth

Hydrides. The hydrides *arsine*, AsH_3, and *stibine*, SbH_3, are both gases which decompose on heating. Bismuth was for a long time considered not to form a hydride, but in 1918 Paneth showed that an unstable volatile hydride could be prepared from radioactive isotopes of bismuth, and small quantities were later prepared by the action of dilute acid on a bismuth-magnesium alloy. It is very unstable and decomposes to liberate bismuth. Both arsine and stibine are prepared together with hydrogen when nascent hydrogen is produced in a solution of one of their salts. They are therefore obtained on adding zinc to a hydrochloric acid solution of arsenic oxide or antimony oxide, or by any other method, such as electrolysis, which produces nascent hydrogen in an arsenic or bismuth solution. The excess hydrogen may be removed by condensing the arsine or stibine in a suitable freezing mixture.

Pure arsine may be prepared by the action of dilute hydrochloric acid on zinc arsenide, Zn_3As_2, the latter being obtained on heating equal weights of arsenic and zinc in a closed crucible,

$$Zn_3As_2 + 6HCl = 2AsH_3 \uparrow + 3ZnCl_2$$

and also by the action of water on sodium arsenide, previously prepared by passing impure arsine over heated sodium—

$$Na_3As + 3H_2O = AsH_3 \uparrow + 3NaOH$$

Pure stibine may be prepared similarly.

Properties. Arsine and stibine are both very poisonous gases, boiling points $-55°C$ and $-17°C$ respectively. Arsine burns in air with a blue flame and white fumes of arsenic trioxide are formed; if the flame is brought into contact with a cool surface however a black deposit of arsenic, which is readily soluble in sodium hypochlorite or bleaching powder solution (distinction from antimony), is obtained. Stibine also burns in air, but the flame is faintly bluish-green in contrast with the vivid flame produced by the arsine and hydrogen mixture, and the dull black antimony deposit which forms on a cool surface is insoluble in the hypochlorite solutions. Both gases decompose on heating and deposit the element as a brown or black mirror, but stibine decomposes at a lower temperature than arsine. This decomposition is the basis of the very delicate Marsh test for detecting and estimating small quantities of arsenic and antimony compounds, particularly in the examination of foodstuffs.

Tests for Arsenic. *Note: These must be carried out in a fume cupboard.*

Marsh's Test. The apparatus is fitted up as in Fig. 222. The U-tube filled with glass-wool moistened with lead acetate serves to remove any sulphuretted hydrogen in the liberated gases, but its value is doubtful and it may be omitted. All reagents must be arsenic-free. Arsenic-free zinc

is placed in the flask and dilute sulphuric acid (1:3) added until hydrogen is evolved vigorously.* The absence of arsenic is verified by passing the hydrogen through a solution of silver nitrate in a suitable container, attached via rubber tubing at *B*; no black precipitate or suspension should be formed. The solution of the arsenic compound is then added to the flask in small quantities at the time, and at the same time the tube is heated at *A* to just below the softening point. A brownish-black mirror of arsenic is deposited in the cooler, less constricted, portion of the tube *beyond A*, due to the thermal decomposition of the arsine. In the case of antimony compounds, a black lustrous mirror is obtained similarly, but in this case it forms on *both* sides of the heated portion of the tube, due to the easier decomposition of stibine compared with arsine. The two mirrors

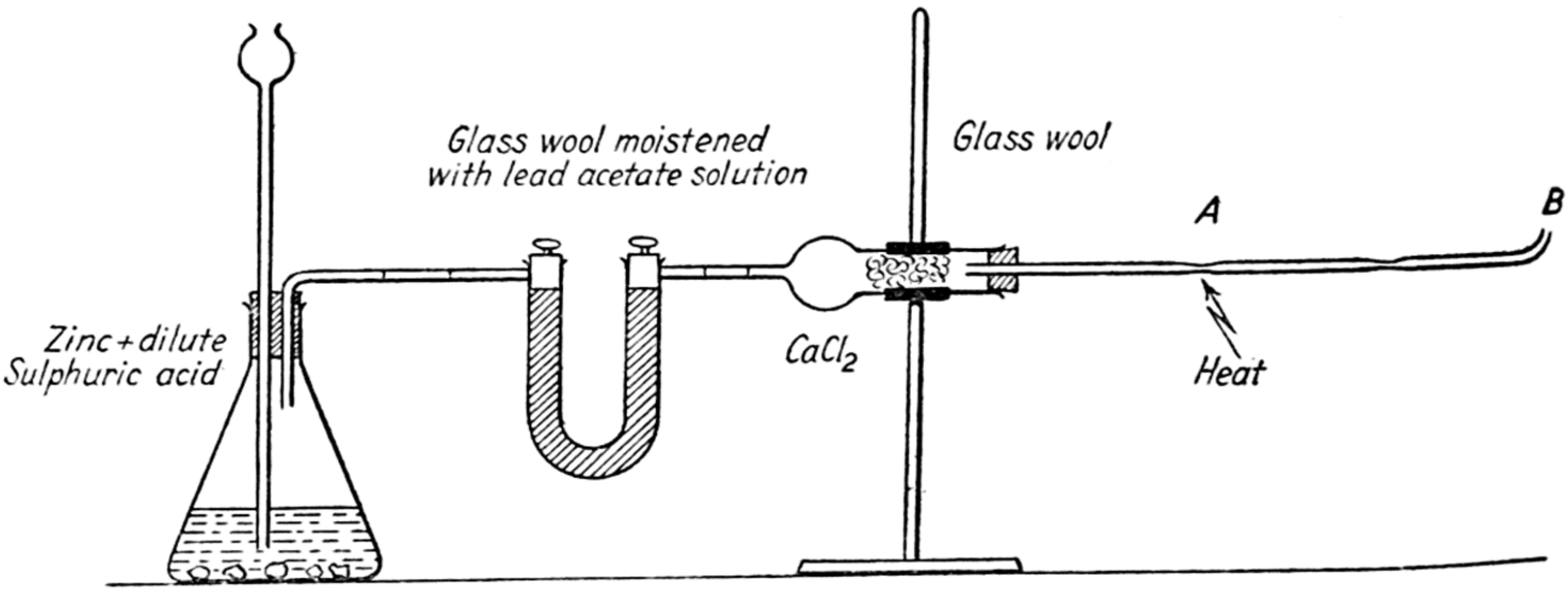


FIG. 222. Marsh Test for Arsenic

may be distinguished by the solubility of arsenic in hypochlorite solutions; antimony is insoluble.

$$2As + 5NaOCl + 3H_2O = 2H_3AsO_4 + 5NaCl$$

In the quantitative estimation of arsenic and antimony by this method, the mirrors are compared with a standard set of mirrors prepared from solutions of known arsenic (and antimony) content. If both arsenic and antimony are present, the assumption is first made that the mirror is arsenic, and after comparing with the standard stains, the arsenic is dissolved out with sodium hypochlorite, and the remaining antimony mirror compared with a set of antimony stains. The arsenic is then found by difference.

Like phosphine, both arsine and stibine are powerful reducing agents, as indicated by their reactions with silver nitrate and mercuric chloride solutions. When arsine is passed into a strong solution of silver nitrate,

* Many analysts nowadays prefer to generate the hydrogen electrolytically, since zinc absolutely free from arsenic is not readily procurable.

a yellow precipitate is first formed of the double compound, $Ag_3As \,.\, 3AgNO_3$, but this slowly changes to form a black precipitate of metallic silver—

$$AsH_3 + 6AgNO_3 = Ag_3As \,.\, 3AgNO_3 \downarrow + 3HNO_3$$
$$Ag_3As \,.\, 3AgNO_3 + 3H_2O = 6Ag \downarrow + 3HNO_3 + H_3AsO_3$$

With dilute silver nitrate, however, the black precipitate of silver forms at once. Note that the filtrate will contain the whole of the arsenic (contrast antimony), and so gives a yellow precipitate of arsenic trisulphide with sulphuretted hydrogen. When stibine is passed into silver nitrate solutions, a black precipitate of silver antimonide, Ag_3Sb, first forms, and this is rapidly decomposed by excess of silver nitrate to give a black precipitate of metallic silver, antimonious oxide and a little free antimony, the precipitate containing the whole of the antimony (contrast arsenic). If the precipitate is dissolved in hot hydrochloric acid or in tartaric acid, and the solution treated with sulphuretted hydrogen, an orange-red precipitate of antimony trisulphide is obtained. These reactions of arsine and of stibine are the basis of the *Gutzeit test*.

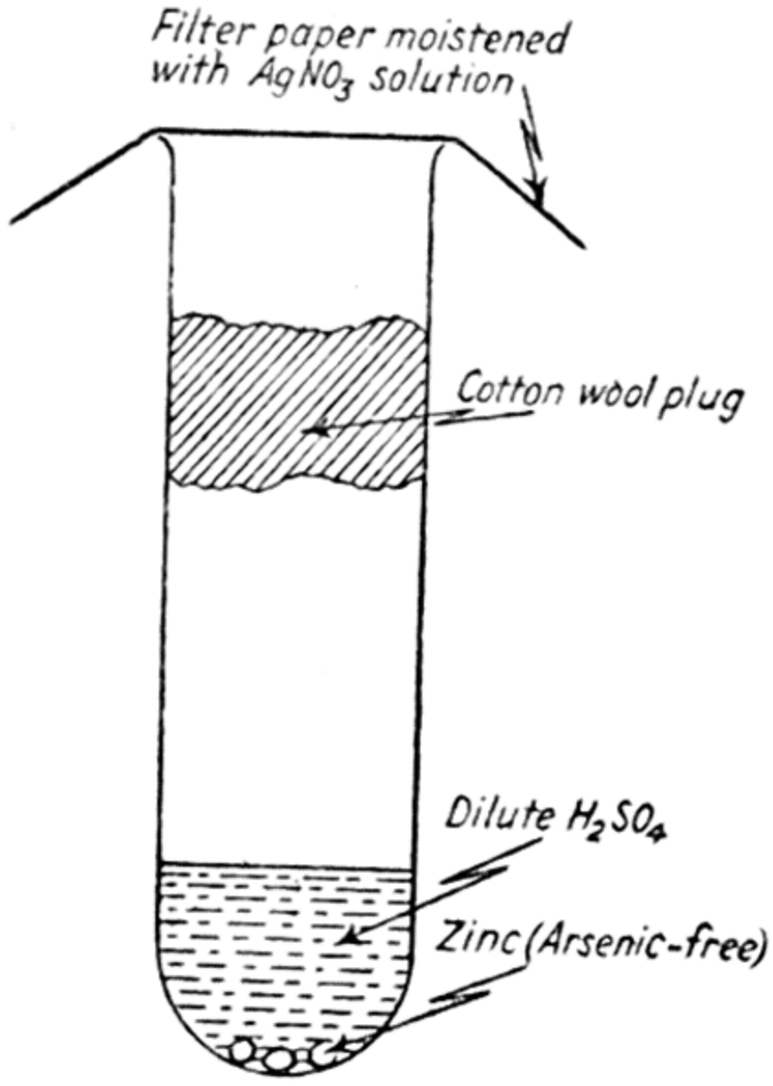


FIG. 223. Gutzeit Test for Arsenic

Gutzeit Test. The apparatus is shown in the accompanying diagram. Arsenic-free zinc and dilute sulphuric acid are placed in the test-tube which is then loosely plugged with purified cotton-wool and covered with a piece of filter-paper moistened with silver nitrate solution. It may be necessary to warm the test-tube slightly to speed up the rate of hydrogen evolution. If after about two minutes no discolouration of the silver nitrate has occurred, the reagents are free from arsenic (and antimony). Usually a light-brown spot is obtained due to traces of impurities. After removing the cotton-wool plug, and adding the arsenic or antimony solution, the cotton-wool plug is replaced and a fresh portion of the silver nitrate paper moved into position over the mouth of the test-tube. The formation of a black precipitate (of metallic silver) indicates arsenic; a brown stain (mainly soluble in 80 per cent alcohol) indicates antimony.

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + 6HNO_3 + H_3AsO_3$$

Nowadays mercuric chloride (or better mercuric bromide) paper is used in place of the silver nitrate; arsenic compounds produce a yellow coloration, but antimony compounds give no stain.

Halogen Compounds

AsF_3 liquid, b. p. 63°C	SbF_3 solid, m. p. 292°C	BiF_3 solid
AsF_5 gas, b. p. − 53°C	SbF_5 liquid, b. p. 155°C	——
$AsCl_3$ liquid, b. p. 132°C	$SbCl_3$ solid, m. p. 73°C	$BiCl_3$ m. p. 227°C
$AsCl_5$ existence doubtful	$SbCl_5$ liquid, b. p. 140°C	——
$AsBr_3$ solid, m. p. 31°C	$SbBr_3$ solid, m. p. 93°C	$BiBr_3$ m. p. 210°C
AsI_3 solid, m. p. 146°C	SbI_3 solid, m. p. 171°C	BiI_3 m. p. 440°C

Trichlorides. These are the most stable chlorides of arsenic, antimony and bismuth and are prepared—

(1) By direct combination of the elements. Reaction occurs on heating, but finely divided arsenic and antimony will ignite spontaneously and burn in chlorine gas—

$$2As + 3Cl_2 = 2AsCl_3$$

(2) By dissolving the trioxide in concentrated hydrochloric acid—

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O$$

(3) By distilling a mixture of the element or its sulphide with mercuric chloride—

$$3HgCl_2 + 2Sb = 2SbCl_3 + 3Hg$$

$$3HgCl_2 + Sb_2S_3 = 2SbCl_3 + 3HgS$$

(4) Bismuth trichloride is also prepared by dissolving bismuth in aqua regia

Arsenic trichloride may be separated by distillation, boiling point 132°C, but antimony and bismuth trichlorides require the higher temperatures of 223°C and 447°C respectively.

Properties. Whereas arsenic trichloride is a colourless viscous liquid, antimony and bismuth trichlorides are both soft white crystalline solids (*butter of antimony*). They are all hydrolyzed by water, but with decreasing readiness in passing from phosphorus to bismuth, in agreement with the increasing metallic character of these elements. Thus phosphorus trichloride fumes in moist air and is immediately hydrolyzed by water; arsenic trichloride is hydrolyzed by excess water and the reaction is reversible—

$$AsCl_3 + 3H_2O \rightleftharpoons H_3AsO_3 + 3HCl$$

Antimony and bismuth trichlorides hydrolyze at ordinary temperatures with excess of water to form oxychlorides, and slowly in boiling water to precipitate the trioxides.

Oxychlorides of Antimony and Bismuth. The reactions—

$$SbCl_3 + H_2O \rightleftharpoons SbOCl\downarrow + 2HCl$$

$$BiCl_3 + H_2O \rightleftharpoons BiOCl\downarrow + 2HCl$$

are reversible. If a solution of the trichloride (or other antimony or bismuth salt in hydrochloric acid) is considerably diluted, for example by pouring a little of the solution into a test-tube of water, a white precipitate of the oxychloride is formed. This redissolves on adding hydrochloric acid, the above reactions being reversed. The formation of the white oxychloride precipitate on diluting the hydrochloric acid solution is often encountered in qualitative analysis, particularly on passing from Group I to Group II, when the solution is diluted to reduce the acid concentration. If such a precipitate forms, the presence of either or both antimony and bismuth in the unknown mixture is indicated.

The oxychlorides are also precipitated on adding a solution of the antimony or bismuth salt to a solution of sodium chloride—

$$Bi(NO_3)_3 + NaCl + H_2O = NaNO_3 + BiOCl\downarrow + 2HNO_3$$

Pentachlorides. Only antimony forms a pentachloride stable at ordinary temperatures. It may be formed by burning antimony in excess of chlorine, by excess of chlorine on the fused trichloride, or by dissolving the trichloride in aqua regia. It is a heavy yellow fuming liquid, which solidifies at 2–4°C and boils at 140°C with some dissociation into the trichloride and free chlorine (cp. PCl_5)—

$$SbCl_5 = SbCl_3 + Cl_2\uparrow$$

With excess of hot water, hydrolysis occurs and a hydrated pentoxide, thought to be antimonic acid, H_3SbO_4, is precipitated.

$$SbCl_5 + 4H_2O = H_3SbO_4 + 5HCl$$

Arsenic pentachloride is thought to be formed by the action of chlorine on the trichloride at very low temperatures, but its existence is very doubtful. Bismuth does not form a pentahalide.

Oxides and Oxy-acids of Arsenic, Antimony and Bismuth

Arsenious Oxide, As_4O_6, is the most important compound of arsenic, being known commercially as "white-arsenic" or simply as "arsenic." It is extremely poisonous, but small doses gradually induce immunity, and it is used medicinally to improve breathing. It is obtained as a white sublimate on roasting arsenical ores, such as pyrites, or by burning arsenic in air (contrast phosphorus which forms the pentoxide)—

$$4FeAsS + 10O_2 = 2Fe_2O_3 + 4SO_2\uparrow + As_4O_6\uparrow$$

It exists in three polymorphous forms—

(*a*) amorphous or vitreous arsenious oxide, m. p. 200°C,
(*b*) octahedral arsenious oxide, which sublimes on heating, and
(*c*) monoclinic arsenious oxide,

and of these, the octahedral form is the most stable. They all vaporize

at 218°C, and are sparingly soluble in water to give a solution which is faintly acidic, presumably due to the formation of arsenious acid, H_3AsO_3, although this acid has never actually been isolated. The amphoteric character of the oxide is revealed by its solution in alkalis or carbonates to form arsenites, and in concentrated hydrochloric acid to form arsenic trichloride; with fuming sulphuric acid an unstable arsenic sulphate is thought to be formed.

$$As_4O_6 + 12NaOH = 4Na_3AsO_3 + 6H_2O$$

$$As_4O_6 + 12HCl \rightleftharpoons 4AsCl_3 + 6H_2O$$

The weakly basic nature of the oxide is revealed by the reversibility of the latter reaction.

Arsenic trioxide is easily reduced to arsenic by heating with charcoal (or potassium cyanide), the arsenic subliming. A brown precipitate of arsenic may be formed by treating the aqueous suspension of the trioxide with reducing agents, such as stannous chloride—

$$As_4O_6 + 6SnCl_2 + 12HCl = 4As + 6SnCl_4 + 6H_2O$$

It may also be oxidized to arsenic pentoxide by oxidizing agents, such as concentrated nitric acid, chlorine and hypochlorites, hydrogen peroxide and ozone, but these reactions are more easily carried out in alkaline solution when the soluble arsenite is oxidized to the soluble arsenate—

$$Na_3AsO_3 + Cl_2 + H_2O = Na_3AsO_4 + 2HCl$$

The corresponding reaction, using iodine as the oxidizing agent, is often used in volumetric analysis, for example, to standardize iodine–potassium iodide solutions, and to estimate hypochlorites such as bleaching powder.

$$Na_3AsO_3 + I_2 + H_2O \rightleftharpoons Na_3AsO_4 + 2HI$$

The above reaction is however reversible, but may be made to go quantitatively from left to right by removing the hydriodic acid as soon as it forms. This is effected by using a solution of sodium arsenite containing excess of sodium bicarbonate; the latter reacts with the hydriodic acid. Sodium hydroxide or sodium carbonate which would otherwise be suitable for this purpose must not however be present since they tend to react with the iodine to form hypoiodites and iodates (*see* p. 814). A standard solution of arsenious oxide is first prepared by dissolving the accurately weighed amount of the trioxide in excess of sodium hydroxide (to form sodium arsenite) and the excess of sodium hydroxide then neutralized by carefully adding sulphuric acid. The solution is then made up to the requisite volume by adding a strong solution of sodium bicarbonate, $NaHCO_3$. Since arsenite solutions are very poisonous, they should always be added from the burette. The end-point of the titration is indicated by the disappearance of the blue colour of the starch-iodine complex.

The reaction with sodium hypochlorite (and bleaching powder) is carried out volumetrically using starch-iodide paper as an external indicator—

$$Na_3AsO_3 + NaOCl = Na_3AsO_4 + NaCl$$
$$NaOCl + 2KI + H_2O = NaCl + 2KOH + I_2$$

Arsenites. Although arsenious acid, H_3AsO_3, has never been isolated, the arsenites are well known. Three series of arsenites exist, and these appear to be derived from the hypothetical acids—

Ortho-arsenious acid, $H_3AsO_3 \rightarrow Na_3AsO_3$, Ag_3AsO_3, etc.
Pyro-arsenious acid, $H_4As_2O_5 \rightarrow Ca_2As_2O_5$, etc.
Meta-arsenious acid, $HAsO_2 \rightarrow NaAsO_2$, $KH(AsO_2)_2$, etc.

The arsenites of the baser metals are insoluble, and include *Scheele's Green*, $CuHAsO_3$, and *Paris Green*, a mixed arsenite and acetate of copper, $Cu\overline{Ac}_2 . 3Cu(AsO_2)_2$. These compounds were formerly used as pigments, particularly for wall-papers, but their use for this purpose has now been discontinued. The growth of certain moulds on the paper produced some very poisonous gaseous organic arsenic compounds, and led to fatal results in several cases. Their main use today is in certain insecticides used in combating plant pests.

Antimony Trioxide, Sb_4O_6, is made by burning antimony in air, or by passing steam over red-hot antimony, or by the hydrolysis of antimony trichloride or sulphate on boiling with water.

$$SbCl_3 + H_2O = SbOCl + 2HCl\uparrow$$
$$4SbOCl + 2H_2O = Sb_4O_6 + 4HCl\uparrow$$

It is a pale buff-coloured solid, practically insoluble in water, and changes reversibly on heating into a yellow polymorphic form. It is readily soluble in dilute hydrochloric acid to form the trichloride, in cold concentrated nitric acid to form the nitrate, $Sb(NO_3)_3$, and in hot concentrated sulphuric acid to form the sulphate, $Sb_2(SO_4)_3$. Its amphoteric properties are shown however by its solution in alkalis to form the meta-antimonites, $NaSbO_2$, derived from the hypothetical meta-antimonious acid, $HSbO_2$. A hydrated form of the trioxide corresponding in composition to ortho-antimonious acid may however be prepared by adding dilute acid to a solution of tartar-emetic, and drying the resulting precipitate at about 100°C.

Tartar-emetic is an important medicinal preparation, having the composition, K(SbO) tartrate, that is, potassium antimonyl tartrate. It is prepared by boiling antimony trioxide with cream of tartar (potassium hydrogen tartrate)

$$4KH \text{ tartrate} + Sb_4O_6 = 4K(SbO) \text{ tartrate} + 2H_2O$$

It is used in small doses, as its name suggests, as an emetic, and also in the treatment of some tropical diseases, and as a mordant in dyeing.

Bismuth Trioxide, Bi_2O_3, is prepared by heating bismuth or any of its other oxides in air, and also by heating its carbonate, nitrate or hydroxide (note resemblance to metals generally). It is easily the most important oxide of bismuth, and is almost exclusively basic. It dissolves easily in acids to form the trivalent bismuth salts, for example, $Bi_2(SO_4)_3$, $Bi(NO_3)_3$, etc., and also forms a series of basic insoluble salts, containing the bismuthyl (BiO) group, for example, BiOCl, bismuthyl chloride, (or bismuth oxychloride), $(BiO)_2SO_4$, etc. Like arsenic and antimony trioxides, bismuth trioxide may easily be reduced to the metal by heating with carbon.

Arsenic Pentoxide, As_4O_{10}, is not formed when arsenic is allowed to burn in air or in oxygen (contrast phosphorus). More vigorous oxidation is necessary, and it is usually prepared by boiling the trioxide with concentrated nitric acid. On cooling the concentrated solution, crystals of ortho-arsenic acid ($2H_3AsO_4 . H_2O$) separate. On heating to about 100°C, the water of hydration is lost to form H_3AsO_4. More vigorous heating for about two hours at 200°C to 230°C produces the pentoxide as a white deliquescent glassy-solid—

$$4H_3AsO_4 = As_4O_{10} + 6H_2O \uparrow$$

At still higher temperatures, for example at red heat, this decomposes to reform the trioxide and liberate oxygen—

$$As_4O_{10} = As_4O_6 + 2O_2 \uparrow$$

Arsenic pentoxide is an acidic oxide, and dissolves in water to form the ortho-arsenic acid. Meta-arsenic acid is unknown (cf. phosphorus), but pyro-arsenic acid exists. Arsenates of all three acids are however formed, and these resemble the corresponding phosphates, both in their method of preparation and in many of their properties, e.g.—

$$2Na_2HAsO_4 \xrightarrow{\text{heat}} Na_4As_2O_7 + H_2O \uparrow$$

$$NaH_2AsO_4 \xrightarrow{\text{heat}} NaAsO_3 + H_2O \uparrow$$

Magnesium ammonium arsenate decomposes on heating to form the pyro-arsenate, a reaction which recalls the similar behaviour of magnesium ammonium phosphate—

$$2Mg(NH_4)AsO_4 = Mg_2As_2O_7 + 2NH_3 \uparrow + H_2O \uparrow$$

This reaction is used in the quantitative determination of arsenates. Nitric acid and ammonium molybdate gives a yellow precipitate of an arseno-molybdate when added to a solution of an arsenate and heated; phosphates react similarly with these reagents but the yellow precipitate of the phospho-molybdate forms in the cold or on very gently warming.

Antimony Pentoxide, Sb_4O_{10}, is obtained as a yellow powder on gently heating the solid obtained by the repeated evaporation of antimony with

concentrated nitric acid. Prepared by this method, it always contains a little of the trioxide, into which it is completely converted on heating to above 440°C. The pentoxide may also be prepared by heating pyro-antimonic acid (*see* below) to about 300°C—

$$2H_4Sb_2O_7 = Sb_4O_{10} + 4H_2O\uparrow$$

Antimony pentoxide is almost insoluble in water. Various hydrated forms of the oxide, corresponding in composition to the ortho-, pyro-, and meta antimonic acids, have been prepared by other methods. Thus hydrolysis of antimony pentachloride by boiling water, followed by drying the resulting precipitate at 100°C, produces the hydrate corresponding to pyro-antimonic acid, $H_4Sb_2O_7$.

$$2SbCl_5 + 7H_2O = 10HCl + H_4Sb_2O_7$$

At 200°C, this hydrate is said to change to the meta-acid, $HSbO_3$, and at 300°C to the pentoxide. Salts of these real, or hypothetical, acids are however known, and of these the pyro-antimonates and meta-antimonates are the most important. These include potassium meta-antimonate, $KSbO_3$, produced by fusing antimony with potassium nitrate, and potassium dihydrogen pyroantimonate, $K_2H_2Sb_2O_7$, which is often used to detect sodium—$Na_2H_2Sb_2O_7$ is only sparingly soluble in cold water and almost insoluble in alcohol.

Bismuth Pentoxide, Bi_2O_5, probably does not exist. It is thought to be formed in an unstable state by the action of chlorine on a concentrated alkaline solution of bismuth trioxide, and also when potassium bismuthate is hydrolyzed by water—

$$2KBiO_3 + H_2O = Bi_2O_5 + 2KOH$$

Sodium Bismuthate, $NaBiO_3$, and **Potassium Bismuthate, $KBiO_3$,** are yellow solids prepared by fusing a mixture of bismuth trioxide and the corresponding alkali with free access of air—

$$2KOH + Bi_2O_3 + O_2 = 2KBiO_3 + H_2O$$

and also by passing chlorine through an alkaline suspension of bismuth trioxide.

They are both powerful oxidizing agents, and are used for this purpose in the detection and estimation of manganese in its salts. Thus, when solid sodium bismuthate is added to a *cold* solution of a manganese salt in dilute nitric acid and the mixture stirred, the characteristic purple colour of the permanganate appears due to the formation of permanganic acid. In quantitative work, the latter is filtered off from the excess sodium bismuthate, and then estimated volumetrically in the usual way.

$$5NaBiO_3 + 2MnSO_4 + 16HNO_3 =$$
$$2HMnO_4 + 5Bi(NO_3)_3 + NaNO_3 + 2Na_2SO_4 + 7H_2O$$

Other oxides of arsenic, antimony and bismuth include As_4O_8 a mixed acid anhydride, Sb_4O_8 a mixed acid anhydride, BiO a dubious bismuth monoxide, and Bi_2O_4 which resembles lead peroxide in its preparation and properties.

The following are the main points of difference and similarity between the oxides and oxy-acids of phosphorus, arsenic, antimony and bismuth—

(*a*) When the element is burnt in air or oxygen, phosphorus forms the pentoxide, whereas arsenic, antimony and bismuth only form the tri-oxides.

(*b*) The pentoxides become decreasingly stable from phosphorus to bismuth. Thus, phosphorus pentoxide, P_4O_{10} is very stable, but the existence of bismuth pentoxide, Bi_2O_5 is doubtful. Whereas the former is obtained simply by burning phosphorus in excess of air, arsenic and antimony pentoxides require more powerful oxidizing agents, and are usually prepared by boiling the corresponding trioxide with concentrated nitric acid.

(*c*) The acids corresponding with ortho-, pyro-, and meta-phosphoric acids similarly become increasingly less definite. Thus ortho- and pyro-arsenic acids appear to have been formed but not the meta-acid; the ortho-, pyro- and meta-antimonic acids appear to exist only as insoluble hydrates of antimony pentoxide; no corresponding bismuthic acids are known.

(*d*) The salts of these acids, whether real or hypothetical, are more definite, and are mainly isomorphous with the corresponding phosphates. Arsenic forms ortho-, pyro- and meta-arsenates, the two latter however being only stable in the solid state; antimony forms meta- and pyro-antimonates but not ortho-antimonates; bismuth forms meta-bismuthates only and these are usually referred to simply as bismuthates.

(*e*) The trioxides become increasingly basic in passing from arsenic to bismuth. Both arsenic and antimony trioxides are amphoteric, but bismuth is almost exclusively basic, with negligible acidic character. The arsenites are less powerful reducing agents than are the phosphites, but they may easily be oxidized to the corresponding arsenates. The antimonites are less stable, and no corresponding bismuth compounds are formed. The increase in basic character of the trioxides is shown by the increasing stability and reluctance of the salts to hydrolyze. Thus, phosphorus trichloride fumes in air, arsenic trichloride forms arsenious acid only slowly with hot water; antimony and bismuth trichlorides are soluble in water, but with excess of the latter, they hydrolyze to form insoluble oxychlorides which are only converted into the insoluble trioxides on prolonged boiling with water. Both antimony and bismuth give stable basic salts containing the antimonyl (SbO) and bismuthyl (BiO) radicals, e.g. K(SbO) tartrate, SbOCl and BiOCl.

Sulphides. The following sulphides of arsenic, antimony and bismuth are known—

Arsenic: As_2S_2 (Realgar), As_2S_3 (Orpiment), and As_2S_5, arsenic pentasulphide.

Antimony: Sb_2S_3 (Stibnite), and Sb_2S_5, antimony pentasulphide.

Bismuth: Bi_2S_3 (Bismuth Glance).

Some, shown with the name of the mineral in brackets, occur in nature and constitute important sources of the parent elements.

Preparation. The general method of preparation is to heat the elements together in the proportions indicated by the formula of the sulphide.

The *trisulphides* are also precipitated on passing sulphuretted hydrogen through solutions of arsenic, antimony and bismuth salts. Arsenic trisulphide is yellow, antimony trisulphide orange-red, and bismuth sulphide brown—

$$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 \downarrow + 6HNO_3$$

The *pentasulphides* of arsenic and antimony are precipitated on acidifying a solution of ammonium thioarsenate or of ammonium thioantimonate (*see* below)—

$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 \text{ (yellow)} \downarrow + 6NH_4Cl + 3H_2S \uparrow$$

$$2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5 \text{ (orange-red)} \downarrow + 6NH_4Cl + 3H_2S \uparrow$$

Properties. Both arsenic trisulphide and antimony trisulphide show acidic properties comparable with arsenic trioxide and antimony trioxide in that they dissolve in the alkali hydroxides, and in ammonium sulphide. Bismuth trisulphide does *not* dissolve in these solutions and this is to be anticipated by the almost exclusively basic nature of bismuth trioxide. The solubility of arsenic trisulphide, but not of antimony trisulphide, in ammonium carbonate similarly reveals the more acidic or non-metallic nature of arsenic compared with antimony.

Arsenic

$$As_2S_3 + 6NaOH = Na_3AsO_3 + Na_3AsS_3 + 3H_2O$$

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$$

$$As_2S_3 + 3(NH_4)_2CO_3 = (NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 3CO_2$$

(Na_3AsO_3 = sodium arsenite; Na_3AsS_3 = sodium thio-arsenite)

Antimony

$$Sb_2S_3 + 6NaOH = Na_3SbO_3 + Na_3SbS_3 + 3H_2O$$

$$Sb_2S_3 + 3(NH_4)_2S = 2(NH_4)_3SbS_3$$

$Sb_2S_3 + (NH_4)_2CO_3$ no reaction

(Na_3SbO_3 = sodium antimonite; Na_3SbS_3 = sodium thio-antimonite)

On acidifying any of the above solutions, the unstable thio-acids are first liberated, but these decompose to precipitate the original trisulphide—

$$2(NH_4)_3AsS_3 + 6HCl = 2H_3AsS_3 + 6NH_4Cl$$
$$2H_3AsS_3 = As_2S_3\downarrow + 3H_2S$$
$$(NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 6HCl = As_2S_3\downarrow + 6NH_4Cl + 3H_2O$$

with similar equations for the thio-antimonites and antimonites.

Arsenic trisulphide and antimony trisulphide are also soluble in yellow ammonium sulphide (that is, ammonium polysulphide) to form ammonium thio-arsenate and ammonium thio-antimonate respectively—

$$As_2S_3 + 3(NH_4)_2S_x = 2(NH_4)_3AsS_4 + \text{sulphur}\downarrow$$
$$Sb_2S_3 + 3(NH_4)_2S_x = 2(NH_4)_3SbS_4 + \text{sulphur}\downarrow$$

On acidifying the solution of these thio-salts, the *penta-sulphides* are precipitated—

$$2(NH_4)_3AsS_4 + 6HCl = 3H_2S\uparrow + As_2S_5\downarrow + 6NH_4Cl$$
$$2(NH_4)_3SbS_4 + 6HCl = 3H_2S\uparrow + Sb_2S_5\downarrow + 6NH_4Cl$$

Arsenic pentasulphide and antimony pentasulphide are also soluble in solutions of caustic alkalis, in colourless and yellow ammonium sulphides, but only the arsenic pentasulphide is soluble in ammonium carbonate.

$$As_2S_5 + 6NaOH = Na_3AsS_4 + Na_3AsO_3S + 3H_2O$$
$$As_2S_5 + 3(NH_4)_2CO_3 = (NH_4)_3AsS_4 + (NH_4)_3AsO_3S + 3CO_2$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4$$

Similar equations apply to the solution of antimony pentasulphide in sodium hydroxide and in ammonium sulphide solutions.

The separation of arsenic trisulphide, antimony trisulphide, and stannous sulphide as Group IIB in qualitative analysis is based on the reactions outlined above. For comparison, the corresponding equations with stannous sulphide are given below, but it should be noted that stannous sulphide does *not* dissolve in colourless ammonium sulphide nor in sodium hydroxide (very slight solubility), but does dissolve in yellow ammonium sulphide due to the formation of a soluble thiostannate—

$$SnS + (NH_4)_2S + S = \underset{\text{thiostannate}}{(NH_4)_2SnS_3}$$

On acidification, a yellow precipitate of stannic sulphide is obtained.

$$(NH_4)_2SnS_3 + 2HCl = SnS_2\downarrow + 2NH_4Cl + H_2S\uparrow$$

TABLE 101

Solubility of Sulphides of Arsenic, Antimony, Bismuth and Tin in Various Solvents

Sulphide	NaOH	$(NH_4)_2S$	$(NH_4)_2CO_3$	$(NH_4)_2S_x$	Conc. HCl
As_2S_3 . . .	Soluble	Soluble	Soluble	Soluble	*Insoluble*
Sb_2S_3 . . .	Soluble	Soluble	*Insoluble*	Soluble	Soluble
SnS . . .	*Slightly soluble*	*Insoluble*	*Insoluble*	Soluble	Soluble
Bi_2S_3 . . .	*Insoluble*	*Insoluble*	*Insoluble*	*Insoluble*	Soluble
As_2S_5 . . .	Soluble	Soluble	Soluble	Soluble	*Insoluble*
Sb_2S_5 . . .	Soluble	Soluble	*Insoluble*	Soluble	Soluble
SnS_2 . . .	Soluble	Soluble	*Insoluble*	Soluble	Soluble

Uses of Arsenic, Antimony and Bismuth

Arsenic. Addition of small quantities of arsenic to copper improve its strength and resistance to oxidation. Arsenical copper is used as sheets for roofing, rain-water gutters, and in certain industrial plant. The addition of about a half per cent of arsenic to lead helps to lower its melting point and improve its hardness; it is used, therefore, in the manufacture of lead shot.

Paris Green (copper aceto-arsenite) is used extensively in mosquito control, but its use in combating the colorado beetle has declined in favour of *lead arsenate* ($PbHAsO_4$) which is a very important insecticide and weed killer. Owing, however, to its potential danger to humans a strict limit has been placed on the amount which can be left on food crops. In the U.S.A., where lead arsenate is extensively used against the codling moth, apple-washing after harvesting has had to be adopted.

Hides for export are treated with salt and *arsenious oxide*, and the latter is also used in many sheep-dips and weed killers, and for preserving wood. Paris Green and Scheele's Green are also used as insecticides and as pigments.

Medicinally important organic arsenic compounds include Salvarsan, Neosalpharsan and Sulpharsphenamine, used principally in combating various tropical diseases and syphilis.

Antimony. The importance of antimony in certain alloys is based on its properties of—

(*a*) Expanding on solidification—hence used to produce type-metals where sharp castings are essential.

TABLE 102

Comparison of Phosphorus, Arsenic, Antimony and Bismuth

	Phosphorus	Arsenic	Antimony	Bismuth
Element	Allotropic (white, violet and black—P)	Allotropic (yellow, grey and black—As)	Allotropic (yellow, black, metallic—Sb)	Not allotropic
Vapour	P_4	As_4	Sb_4	Bi_2
Reactivity	Very reactive → decreasing reactivity			
	Non-metal → increasing metallic character			
Air	Burns → P_4O_{10}	Burns → As_4O_8	Burns → Sb_4O_8	Combines → Bi_2O_3
Chlorine	Burns → PCl_5	Burns → $AsCl_3$	Burns → $SbCl_3$	Combines → $BiCl_3$
Conc. HNO_3	→ H_3PO_4	→ H_3AsO_4	→ Sb_4O_{10}	→ $Bi(NO_3)_3$
Hydrides	PH_3, feebly basic, very poisonous → phosphides	AsH_3, neutral, very poisonous → arsenides, (Zn_3As_2, Na_3As)	SbH_3, neutral very poisonous and less stable	BiH_3 prepared only in very small quantities, very unstable
	Powerful reducing agents, e.g. $AgNO_3$ → Ag			
	Decomposes on heating → decreasing stability			
Chlorides	PCl_5 dissoc. on heating	$AsCl_5$ stable only at low temperatures	$SbCl_5$ dissoc. on heating, like PCl_5	$BiCl_5$ *not* formed
	PCl_3	$AsCl_3$	$SbCl_3$	$BiCl_3$
	Increasing salt-like character →			

	Fumes in air, forming phosphorous acid on hydrolysis	Hydrolyzed slowly at ordinary temperature → As_2O_3	With excess of water → SbOCl, which → Sb_2O_3 on boiling	With excess of water → BiOCl
Oxides	P_4O_{10} formed when W.P. burns in excess of oxygen	As_4O_{10} and Sb_4O_{10} *not* formed when As and Sb are burnt in air (→ As_4O_6 and → Sb_4O_6)		Bi_2O_5 existence doubtful
	H_3PO_4, $H_4P_2O_7$, HPO_3 acids and salts occur	H_3AsO_4, $H_4As_2O_7$ but *not* $HAsO_3$; but salts of all three acids occur	Acids are very doubtful, but pyro- and meta-antimonates occur	No corresponding acids; meta-bismuthates occur, e.g. $KBiO_3$.
	P_4O_6	As_4O_6	Sb_4O_6	Bi_2O_3
	Acidic character decreases →			
	H_3PO_3 and phosphites formed	H_3AsO_3 not isolated, but ortho-, pyro-, and meta-arsenites occur	H_3SbO_3 doubtful, but meta-antimonites occur	Forms no acids or bismuthites
	Basic character increases →			
	Not basic	Amphoteric, but more acidic than basic	Amphoteric, but more basic than acidic	Basic only
	PCl_3 immediately hydrolyzed by water	$AsCl_3$ slowly hydrolyzed	$SbCl_3$, $Sb(NO_3)_3$ etc. and basic antimonyl salts occur, e.g. SbOCl	$BiCl_3$, etc., and basic bismuthyl salts occur, e.g. BiOCl
Sulphides	P_4S_3, P_2S_5, and P_4S_7 Hydrolyzed by water	As_2S_2, As_2S_3, and As_2S_5 Soluble in NaOH etc.	Sb_2S_3, Sb_2S_5. Soluble in NaOH, etc.	Bi_2S_3. Soluble only in acids

(*b*) Hardening the base metal—hence used to produce certain bearing alloys, for example Babbitt metal which contains very hard crystals of an intermetallic compound, such as SnSb.

Examples of these alloys are given in Table 103.

TABLE 103

Some Antimony Alloys

Alloy*	Tin	Lead	Antimony	Copper
Type metal . .	5	75	20	—
Pewter . . .	83–75	0–20	0–7	2
Britannia metal .	93·3	—	4·6	2
Babbitt metal . .	83·3	—	8·3	8·3

* Percentage composition by weight

Antimony White (Sb_2O_3) is used as a paint pigment, and the most important organic compound of antimony used medicinally is *Stibophen*, which is used in the treatment of certain parasitic diseases common in India and some Eastern Mediterranean districts.

Bismuth is used principally in the manufacture of fusible metal alloys, which find many uses based on their relatively low softening or melting points, for example in the control of fire hazards. These alloys are employed for safety plugs in steam boilers, in electrical fire alarms and in automatic sprinklers to be seen in all large buildings. In the following Table are given the more important of these alloys with their melting points.

TABLE 104

Some Bismuth Alloys

Alloy*	Tin	Lead	Bismuth	Cadmium	Melting Point
Newton's metal .	3	5	8	–	94·5°C
Rose's fusible metal .	1	1	2	–	93·75°C
Wood's fusible metal.	1	2	4	1	65°–68°C

* Percentage composition by weight

Detection and Estimation of Arsenic, Antimony and Bismuth. Qualitatively, arsenic, antimony and bismuth are precipitated as their sulphides in Group II on passing sulphuretted hydrogen into their acid solution. The

solubility of arsenic and antimony sulphides in yellow ammonium sulphide permits their separation from bismuth (and other Group IIA) sulphides. Sulphides of arsenic and antimony are reprecipitated with dilute hydrochloric acid, and then separated by boiling with concentrated hydrochloric acid which dissolves the antimony sulphide. The formation of the oxychlorides of antimony and of bismuth on pouring a little of the hydrochloric acid solution into water are useful pointers to the presence of these elements.

A more delicate test for bismuth is the production of a black precipitate or colouration when a freshly prepared solution of sodium stannite is poured over the bismuth hydroxide precipitated in the Group IIA separation.

Small quantities of arsenic and of antimony are detected by the Marsh and Gutzeit tests (*see* p. 697).

Arsenates are detected by the formation of a yellow precipitate on heating the solution obtained after adding nitric acid and ammonium molybdate and also by the formation of a chocolate-brown precipitate when silver nitrate is added to a neutral solution of the arsenate.

Quantitatively, arsenic is determined by conversion into the arsenate, for example by treatment with nitric acid, and then adding ammonium chloride, ammonium hydroxide and magnesium chloride solutions to precipitate magnesium ammonium arsenate, $Mg(NH_4)AsO_4$. This is collected, dried and weighed in this form, or preferably is ignited to the pyro-arsenate before weighing—

$$2Mg(NH_4)AsO_4 = Mg_2As_2O_7 \downarrow + 2NH_3 \uparrow + H_2O \uparrow$$

Antimony is usually determined as the sulphide, Sb_2S_3, which is collected, dried and weighed, whilst bismuth is precipitated as its carbonate, which is then ignited and weighed as the oxide, Bi_2O_3.

$$2Sb(NO_3)_3 + 3H_2S = Sb_2S_3 \downarrow + 6HNO_3$$

$$2Bi(NO_3)_3 + 3Na_2CO_3 = Bi_2(CO_3)_3 \downarrow + 6NaNO_3$$

$$Bi_2(CO_3)_3 = Bi_2O_3 + 3CO_2$$

CHAPTER 24

THE ELEMENTS OF GROUP VI

THE Group VI family of elements include—

Oxygen—Sulphur
- Chromium—Molybdenum—Tungsten (Sub-group A)
- Selenium—Tellurium—(Sub-group B)

The chemistry of oxygen has already been discussed in detail in Chapter 17, and before proceeding to the study of the remaining elements of the Group, it is proposed to discuss the chemistry of two important compounds which contain oxygen. These are hydrogen peroxide and ozone.

HYDROGEN PEROXIDE

A solution of hydrogen peroxide was first prepared by Thénard in 1818 by the action of dilute sulphuric acid on barium peroxide—

$$BaO_2 + H_2SO_4 = BaSO_4\downarrow + H_2O_2$$

Since then, its importance has increased considerably, particularly so during the last World War when its value as a fuel for gas-turbine engines used in rockets, torpedoes, etc., was discovered and exploited by the Germans.

Hydrogen peroxide is formed in small quantities in many reactions in which *atomic* hydrogen is liberated in the presence of oxygen, the following reaction then taking place—

$$H + O{=}O + H \rightarrow H{-}O{-}O{-}H$$

Thus small quantities are produced—

(*a*) By bubbling oxygen about an electrode at which hydrogen is being liberated during electrolysis.

(*b*) When hydrogen burns in air, for example, with the jet of burning hydrogen impinging on the surface of cold water, or of ice-water.

(*c*) By passing a high-frequency electric discharge through a gaseous mixture of hydrogen and oxygen.

Laboratory Preparation. The usual method, involving the use of barium peroxide, occurs in two stages—

(*a*) Preparation of hydrated barium peroxide, $BaO_2 . 8H_2O$.

(*b*) Action of cold dilute sulphuric acid on this hydrated peroxide.

Anhydrous barium peroxide is not easily decomposed by dilute sulphuric acid due to the formation of a protective coating of insoluble

barium sulphate on the peroxide particles. The hydrated barium peroxide, however, is readily decomposed by this acid. Commercial barium peroxide is therefore first converted into its hydrate by the following procedure. The finely powdered peroxide is added a little at a time to a cold mixture of equal volumes of water and concentrated hydrochloric acid until the latter is neutralized—

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2$$

A little barium hydroxide solution is then added to precipitate iron and aluminium impurities as their hydroxides. These, together with the silica originally present as impurity in the barium peroxide, are filtered off, and the filtrate then added to a saturated solution of barium hydroxide—

$$H_2O_2 + Ba(OH)_2 + 6H_2O = BaO_2 \,.\, 8H_2O \downarrow$$

The precipitated hydrated barium peroxide is then filtered off, washed with cold water free from carbon dioxide, and kept moist in a stoppered bottle.

Hydrogen peroxide is then prepared from this hydrated barium peroxide by treatment with *cold dilute* sulphuric acid. The barium is precipitated as barium sulphate leaving a solution containing only hydrogen peroxide—

$$BaO_2 + H_2SO_4 = BaSO_4 \downarrow + H_2O_2$$

A convenient laboratory method for preparing small quantities of hydrogen peroxide is to add small quantities of sodium peroxide to ice-water. (Since sodium peroxide sometimes contains unchanged metallic sodium, which will liberate hydrogen by reaction with the water, it is advisable not to apply a light to the gas evolved from the mixture.)

$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2$$

Commercial Preparation. The method used by Thénard is still an important commercial method for preparing hydrogen peroxide solutions, but the use of sulphuric acid to decompose the barium peroxide is avoided because it catalyzes the decomposition of the hydrogen peroxide. Acids such as phosphoric acid, or carbonic acid, are preferred.

The barium peroxide is obtained from the mineral barytes ($BaSO_4$) by the following sequence of reactions—

(i) Roasting an intimate mixture of barytes with coke in a rotary kiln—

$$BaSO_4 + 4C = BaS + 4CO \uparrow$$

(ii) The barium sulphide is then converted into barium carbonate by treatment with an aqueous solution of sodium carbonate—

$$BaS + Na_2CO_3 = BaCO_3 \downarrow + Na_2S$$

(iii) Heating the precipitated barium carbonate with carbon—

$$BaCO_3 + C = BaO + 2CO \uparrow$$

(iv) Heating the resulting barium monoxide in a stream of purified air at 540°C—

$$2BaO + O_2 = 2BaO_2$$

In the *phosphoric acid-sulphuric acid method*, the barium peroxide is treated with a solution of phosphoric acid, and the precipitate of barium phosphate separated—

$$3BaO_2 + 2H_3PO_4 = Ba_3(PO_4)_2 \downarrow + 3H_2O_2$$

The phosphoric acid is recovered for further use by first dissolving the barium phosphate in more phosphoric acid, and then adding sulphuric acid to precipitate barium sulphate—

$$Ba_3(PO_4)_2 + 4H_3PO_4 = 3Ba(HPO_4)_2$$
$$3Ba(HPO_4)_2 + 3H_2SO_4 = 3BaSO_4 \downarrow + 6H_2PO_4$$

A second method for preparing hydrogen peroxide from barium peroxide is to pass a stream of carbon dioxide gas into cold water to which the barium peroxide is slowly added—

$$BaO_2 + CO_2 + H_2O = BaCO_3 \downarrow + H_2O_2$$

The inter-war years saw the development of the very important process by which hydrogen peroxide is obtained *from persulphuric acid*. When a solution of the latter is steam-distilled, the following reaction occurs to produce a solution of hydrogen peroxide as distillate—

$$H_2S_2O_8 + 2H_2O = 2H_2SO_4 + H_2O_2 \uparrow$$

The persulphuric acid was formerly prepared directly by the electrolysis of a fairly concentrated solution of sulphuric acid, the following reaction occurring at the anode—

$$HSO_4^- \rightarrow (HSO_4) + e$$
$$2(HSO_4) \rightarrow H_2S_2O_8$$

Nowadays persulphuric acid is prepared indirectly. A solution of ammonium hydrogen sulphate is electrolyzed to form a solution of ammonium persulphate. The precipitate of potassium persulphate formed on subsequently adding potassium hydrogen sulphate is separated, and then acidified to liberate the persulphuric acid—

$$(NH_4)_2S_2O_8 + 2KHSO_4 = K_2S_2O_8 \downarrow + 2(NH_4)HSO_4$$
$$K_2S_2O_8 + 2H_2SO_4 = 2KHSO_4 + H_2S_2O_8$$

Alternatively, in the *Kurfstein process*, the ammonium persulphate,

prepared as above by the electrolysis of ammonium hydrogen sulphate, is steam-distilled directly, that is, without first liberating persulphuric acid—

$$(NH_4)_2S_2O_8 + 2H_2O = 2NH_4HSO_4 + H_2O_2 \uparrow$$

A newer process, not yet carried out on a large scale in this country, passes a mixture of hydrogen and oxygen (19 to 1, by volume) saturated with water vapour, between two parallel quartz plates each coated with aluminium on its outer side. A high-voltage, high-frequency electric discharge is then passed between the plates to produce small quantities of hydrogen peroxide.

Concentration of Hydrogen Peroxide Solutions. For most normal purposes a solution of about 30 per cent concentration may be prepared by concentrating the aqueous solutions prepared by the above methods by evaporation on a water-bath at about 70°C, but for more concentrated solutions, it is necessary to distill the hydrogen peroxide. At 100°C, however, hydrogen peroxide solution decomposes rapidly, so that the method of distilling at ordinary atmospheric pressure is useless. If, however, the pressure is reduced, the boiling point is also lowered, and if the pressure is reduced sufficiently the boiling point of the hydrogen peroxide solution will be reduced below the temperature at which it begins to show appreciable decomposition. This is the basis of the method for preparing solutions up to about 90 per cent hydrogen peroxide concentration. At 15 mm Hg pressure, for example, the hydrogen peroxide distils over at about 35–40°C, at which temperature very little decomposition occurs. These concentrated solutions are often stabilized with sodium pyrophosphate or phosphoric acid, and stored in containers of a special stainless steel. Hydrogen peroxide of 100 per cent concentration is now a commercial product.

Properties of Hydrogen Peroxide. Solutions of hydrogen peroxide are colourless, indistinguishable from water in appearance, unless the solution is very concentrated when it is somewhat viscous, and slightly blue in colour when seen in bulk. The highest concentration solution manufactured nowadays contains up to 100 per cent hydrogen peroxide, but most commercially available solutions are weaker. These include the "10, 20, 40 and 100-volume" solutions, and "perhydrol" which contains about 30 per cent hydrogen peroxide. The "volume-strength" of a hydrogen peroxide solution expresses the concentration in terms of the number of volumes of oxygen gas which would be produced by the complete decomposition of one volume of the given hydrogen peroxide solution.

$$2H_2O_2 = 2H_2O + O_2 \uparrow$$

Thus, 1 ml of a "100-volume solution" will produce 100 ml of oxygen gas on complete decomposition. The term is of theoretical rather than of practical importance, since it is usually determined indirectly from a

knowledge of the amount of hydrogen peroxide contained in the given solution (*see*, for example, p. 722).

Concentrated solutions of hydrogen peroxide should not be allowed to come into contact with the skin since painful white blisters are produced, but weak solutions are much used for antiseptic purposes in hospitals and as a mouth wash. The action of the concentrated solution on the skin is paralleled by its behaviour on certain organic compounds. Solutions of concentrated hydrogen peroxide which contain alcohols, ketones, or sugars, etc., are relatively stable when left undisturbed, but under some conditions reactions may develop with explosive violence. Precaution is also taken to prevent concentrated hydrogen peroxide solution from coming into contact with inflammable material. The decomposition of a 65 per cent solution produces just enough heat to evaporate all the water normally contained in the material, so that with solutions of higher concentration, ignition, and continuing fires are produced.

Decomposition. Hydrogen peroxide is remarkable for the number and variety of substances which catalyze its decomposition, and also for the very large effect produced in many cases by even minute quantities of these substances. Thus a little platinum black produces explosive decomposition, and similar decomposition occurs with other finely divided metals, such as copper, gold, etc. In general, only those metals which may occur in two or more valency states appear to catalyze the decomposition. Almost all forms of dust and dirt catalyze the decomposition, as also do many ferments and enzymes, provided that in the latter cases, the solution of hydrogen peroxide is not too concentrated to kill them before appreciable decomposition occurs. Substances such as manganese dioxide, and sodium and potassium permanganates are also very effective catalysts.

In the absence of impurities, such as have been outlined in the preceding paragraph, solutions of hydrogen peroxide, even the 90 to 100 per cent solution, are unexpectedly very stable and may even be transported in bulk. Usually, however, stabilizers are added, and these may belong to one or both of the following two categories—

(*a*) *Acids*. Hydrogen peroxide solutions are more stable when acid than when alkaline, and acids, such as phosphoric acid, are often added as stabilizers. The stronger mineral acids, such as sulphuric acid, are not stabilizers however.

(*b*) *Anti-decomposition catalysts*. Substances, such as pyrophosphates, and fluorides are often added as stabilizers, and these probably owe their activity to their action with (or, otherwise rendering inactive of) any decomposition catalysts which may be present. Substances such as freshly precipitated alumina or silica probably remove these decomposition catalysts by an adsorption process. One of the best commonly applied stabilizers is acetanilide.

There is, however, no single "best" stabilizer for hydrogen peroxide

solutions, and the most satisfactory guarantee of stability is the freedom of the peroxide from all impurities.

The decomposition of hydrogen peroxide is strongly exothermic—

$$\underset{\text{liquid}}{2H_2O_2} = \underset{\text{liquid}}{2H_2O} + O_2 + 46\,900 \text{ cal.}$$

One litre of 90 per cent hydrogen peroxide on complete decomposition produces 589 g of oxygen and 801 g of steam. If the decomposition is carried out under adiabatic conditions (that is, with no escape of heat to the surroundings), the resulting temperature (as calculated) is about 750°C, and the total volume of gas produced, measured at the same temperature and at atmospheric pressure, is the very considerable one of about 5000 litres and this considerable and rapid evolution of gas may be used for propellent purposes. In practice this rapid decomposition of a concentrated solution of hydrogen peroxide is effected by the use of small quantities of a decomposition catalyst, such as manganese dioxide, or sodium (or potassium) permanganate.

The first practical application of concentrated hydrogen peroxide in this new role as a potential source of power was to use the resulting oxygen-steam mixture to drive a gas-turbine engine. Later improvements increased still further the motive power by injecting a liquid fuel, such as alcohol, into the oxygen-steam mixture. The resulting very rapid oxidation of the alcohol not only generates more heat but also increases the total volume of the issuing gases—

$$\underset{\text{liquid}}{C_2H_5OH} + 3O_2 = 2CO_2\uparrow + \underset{\text{steam}}{3H_2O\uparrow}$$

This hydrogen peroxide-liquid fuel combination was used by the Germans to provide jet propulsion in their V-2 rockets, etc., and towards the closing stages of the last War, 5000 h.p. gas-turbine engines were developed which would have been capable, for example, of driving a submarine under water without producing a gas-bubble wake, since the products of the reactions (CO_2 and H_2O) are themselves soluble.

Oxidizing Properties of Hydrogen Peroxide. Apart from the violent nature of the reactions which may occur with concentrated hydrogen peroxide solutions, the weaker aqueous solutions are also powerful oxidizing agents, but with the difference that there is no hazard in the use of the latter. A solution of hydrogen peroxide is particularly effective as an oxidizing agent when catalyzed by adding a small quantity of ferrous sulphate, although mineral acids also accelerate its oxidizing properties. The basic equation for the behaviour of hydrogen peroxide in oxidation reactions may be considered to be—

$$H_2O_2 \rightarrow H_2O + \overline{O}$$

and the oxidizing properties considered to result from the additional atom of oxygen which the molecule of hydrogen peroxide possesses over that of water.

Examples of hydrogen peroxide as an oxidizing agent include—

(*a*) With acidified potassium iodide, iodine is liberated—

$$H_2O_2 + 2HI = 2H_2O + I_2\downarrow$$

(*b*) Black lead sulphide is converted into lead sulphate (white)—

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

and this reaction is used to clean oil-paintings in which the white lead pigments have become darkened by sulphur compounds, such as sulphuretted hydrogen, in the atmosphere.

In general, when hydrogen peroxide behaves as an oxidizing agent on an inorganic compound dissolved in water, the resulting oxidation-reaction belongs to one of the following three types—

(*a*) *Change in valency*. Examples of this type of reactivity are contained in the following equations--

$$\underset{\text{sodium arsenite}}{Na_3AsO_3} + H_2O_2 = \underset{\text{sodium arsenate}}{Na_3AsO_4} + H_2O$$

$$Na_2SO_3 + H_2O_2 = Na_2SO_4 + H_2O$$

$$2FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2H_2O$$

$$\underset{\text{chromic hydroxide}}{2Cr(OH)_3} + 3H_2O_2 = \underset{\text{chromic acid}}{2H_2CrO_4} + 4H_2O$$

(*b*) *Formation of a "peroxide" bond*, —O—O—, without change of valency. Examples of this type of reactivity include the formation of barium peroxide with barium hydroxide—

$$Ba(OH)_2 + H_2O_2 = Ba\begin{matrix}O\\|\\O\end{matrix} + 2H_2O$$

and also the formation of pertitanates, permolybdates and perchromates. When hydrogen peroxide is added to an acidified solution of potassium dichromate, an *unstable perchromic acid* is produced. If the reaction is repeated in the presence of a little ether, then, after shaking and allowing the ether to separate as the upper layer, it will be found to have a beautiful blue colour, due to dissolved perchromic acid. This reaction is sufficiently sensitive to detect 0·1 milligrammes of hydrogen peroxide. Similarly, if hydrogen peroxide is added to a slightly acid solution of titanium sulphate, $Ti(SO_4)_2$, a yellow or orange-red coloration is produced, depending on the concentration of the hydrogen peroxide. This colour is due to the formation of a *pertitanic acid*, $H_2[TiO_2(SO_4)_2]$, and not as was originally supposed to the formation of a higher titanium oxide, such as TiO_3. This

is an extremely delicate test for hydrogen peroxide, being sensitive to about one part in 25 000 parts of water.

(*c*) *Formation of an addition-compound.* When hydrogen peroxide is added to an aqueous solution of borax, the compound known as sodium perborate is formed. It is not, however, a true per-compound, but contains a molecule of hydrogen peroxide in very much the same way as hydrates contain molecules of water. Its structure is considered to be $NaBO_2 . H_2O_2 . 3H_2O$. When it is heated in aqueous or acid solution, it liberates oxygen.

Reducing Properties of Hydrogen Peroxide. It has been said that hydrogen peroxide behaves as an oxidizing agent by virtue of the reaction—

$$H_2O_2 = H_2O + \overline{O}$$

The $\overline{O}$ is the effective agent which oxidizes (and is therefore absorbed by) the other substance, so that no oxygen gas is liberated. Hydrogen peroxide also reacts with certain compounds which are themselves oxidizing agents, and in these reactions, the hydrogen peroxide *apparently* behaves as a reducing agent. In all these reactions, however, oxygen is evolved as a gas, and it therefore appears more correctly that the odd oxygen atom of the hydrogen peroxide molecule oxidizes the odd oxygen atoms of the other oxidizing agents, as for example in its reaction with ozone—

$$O{=}O{-}\boxed{{\rightarrow}O + O{\leftarrow}}{-}O\begin{matrix}H\\ \diagup\\ \diagdown\\ H\end{matrix} = O_2 + O_2 + H_2O$$

Other reactions of this type include—

(*a*) Oxides of silver, gold, manganese, etc., are reduced to the metal—

$$Ag_2O + H_2O_2 = 2Ag\downarrow + H_2O + O_2\uparrow$$

$$Au_2O_3 + 3H_2O_2 = 2Au\downarrow + 3H_2O + 3O_2\uparrow$$

If hydrogen peroxide is added to a solution of gold chloride, a colloidal solution of very finely divided gold is obtained, which appears greenish-blue by transmitted light, and brown by reflected light—

$$2AuCl_3 + 3H_2O_2 = 2Au + 6HCl + 3O_2\uparrow$$

(*b*) Manganese dioxide and lead dioxide are similarly reduced in acid solution—

$$MnO_2 + H_2SO_4 + H_2O_2 = MnSO_4 + 2H_2O + O_2\uparrow$$

$$PbO_2 + H_2O_2 = PbO + H_2O + O_2\uparrow$$

In alkaline solution, however, manganous oxide is oxidized to manganese dioxide.

(*c*) A solution of potassium permanganate in acid solution is rapidly

decolorized by a solution of hydrogen peroxide with evolution of oxygen—

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5\overline{O}$$
$$5H_2O_2 + 5\overline{O} = 5H_2O + 5O_2\uparrow$$
$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2\uparrow$$

The net reaction, as described in the last equation, offers a convenient method for determining the concentration of hydrogen peroxide solutions by the methods of volumetric analysis. Standard potassium permanganate solution is run in from the burette into a measured volume of the hydrogen peroxide solution to which sulphuric acid has been added. The end-point of the titration is indicated by the first appearance of a permanent pink coloration.

(*d*) A solution of potassium ferricyanide in acid solution is reduced to potassium ferrocyanide when treated with hydrogen peroxide. Oxygen is liberated at the same time—

$$2H_3[Fe(CN)_6] + H_2O_2 = 2H_4[Fe(CN)_6] + \overline{O}$$
$$H_2O_2 + \overline{O} = H_2O + O_2$$
$$2H_3[Fe(CN)_6] + H_2O_2 = 2H_4[Fe(CN)_6] + O_2\uparrow$$

Detection of Hydrogen Peroxide

(*a*) *Perchromic Acid Test.* A few drops of potassium dichromate solution are added to an acidified solution of hydrogen peroxide and ether, and the mixture gently shaken. The ether is then allowed to separate as an upper layer, which is blue in colour.

(*b*) *Titanium Sulphate Test.* Hydrogen peroxide added to a solution of titanium sulphate produces a yellow to orange-red coloration depending on the concentration of the hydrogen peroxide. The titanium sulphate reagent may be prepared by fusing titanium dioxide, TiO_2, with potassium bisulphate, cooling, and dissolving in water.

(*c*) *Potassium Permanganate Test.* Hydrogen peroxide decolorizes an acid solution of potassium permanganate in the cold with evolution of oxygen.

(*d*) *Lead Sulphide Test.* Hydrogen peroxide oxidizes lead sulphide which is black in colour to the white lead sulphate. The test is most easily carried out by drop-wise addition of the hydrogen peroxide to a test-paper impregnated with lead sulphide.

Determination of Hydrogen Peroxide "Strength." The hydrogen peroxide solution, if necessary diluted in a definite ratio, is acidified with sulphuric acid and titrated against a standard solution of potassium permanganate as described above. The normality of the diluted hydrogen peroxide solution is then calculated in the usual way. Let it be 0·1 N.

The fundamental equation—

$$H_2O_2 = H_2O] + \overline{O}$$

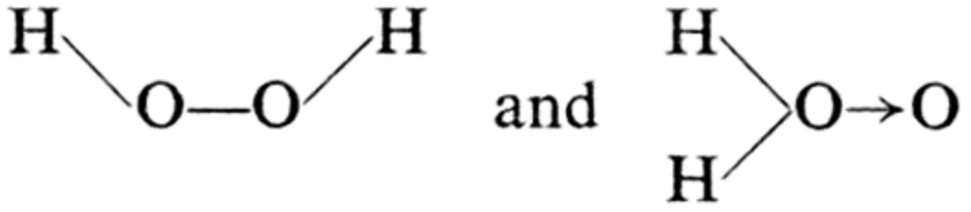
shows that one molecule of H_2O_2 is equivalent to one atom of oxygen (and hence to two atoms of hydrogen), so that a normal solution of hydrogen peroxide contains 17 g of the latter per litre. The 0·1 N solution therefore contains 1·7 g H_2O_2 per litre.

The reaction involved in the expression "volume strength" is—

$$2H_2O_2 = 2H_2O + O_2\uparrow$$

from which it is seen that 68 g of hydrogen peroxide can produce 22·4 litres of oxygen gas, measured at S.T.P., on complete decomposition. Therefore, a litre of 0·1 N hydrogen peroxide will produce $\frac{22{\cdot}4}{68} \times 1{\cdot}7 = 0{\cdot}56$ litres of oxygen under the same conditions. If the original hydrogen peroxide solution was diluted to n times its original volume, then $0{\cdot}56n$ litres of oxygen would be produced by the complete decomposition of one litre of the original solution, so that its volume strength is "$0{\cdot}56n$."

Formula of Hydrogen Peroxide. The following two formulae have been suggested for hydrogen peroxide—



(I) (II)

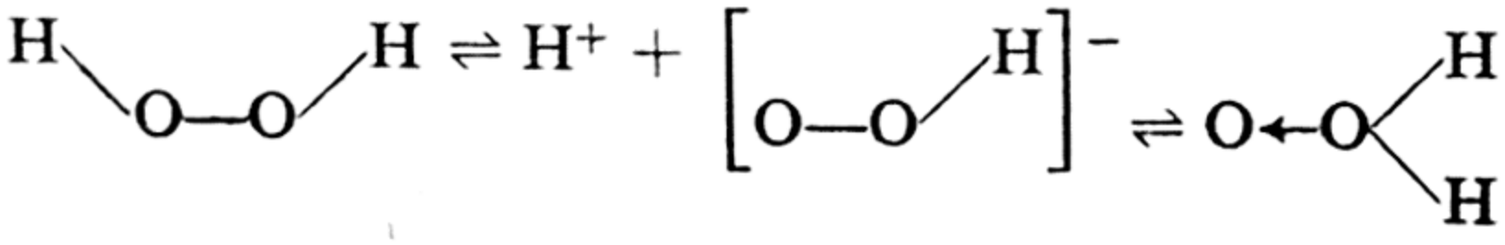
Formula I has now been established as the true formula for *anhydrous* hydrogen peroxide. Thus, chlorosulphonic acid reacts smoothly with anhydrous hydrogen peroxide to form perdisulphuric acid, which has the peroxide structure, as revealed by X-ray crystal structure analysis of potassium persulphate.

$$HO\,.\,O_2S\text{–}\boxed{\text{–Cl + H–}}\text{–O—O–}\boxed{\text{–H + Cl–}}\text{–}SO_2OH$$

$$\rightarrow HO\,.\,O_2S\text{—O—O—}SO_2OH + 2HCl$$

Measurements of the dipole moments, and examination of the infra-red absorption spectrum of anhydrous hydrogen peroxide both confirm formula I, and have shown that the structure consists of a skewed arrangement of the hydrogen and oxygen atoms, that is, the molecule is both non-linear and non-planar.

Formula II. In *aqueous solution*, the following tautomeric equilibria probably occur, as a result of the feeble ionization of the $(HO_2)^-$ anion—



so that both forms of hydrogen peroxide probably occur in aqueous solutions. Note that both forms produce the same anion $(HO_2)^-$.

Uses of Hydrogen Peroxide. Concentrated solutions (about 90 per cent) are used in conjunction with liquid fuels such as methyl alcohol and hydrazine hydrate and suitable decomposition catalysts to provide power for "jet" propulsion in rockets, torpedoes, etc. Smaller quantities are used in certain explosive compositions.

The weaker commercial solutions find many uses such as—

(*a*) Antiseptic purposes in hospitals (treatment of wounds, etc.) and in many toilet preparations. Peroxides, perborates and persulphates find similar usage.

(*b*) As a bleaching agent, particularly for wool and other animal fibres, (furs, etc.), for which large quantities are required.

(*c*) In the treatment of paintings and other works of art which have darkened due to the conversion of the lead pigments into black lead sulphide.

(*d*) To prevent milk turning sour. The addition of quite small quantities of hydrogen peroxide to keep milk fresh during hot and thundery weather has not yet been adopted in this country, although it is practised in such countries as Italy. Stabilizers, such as fluorides should of course be absent from the hydrogen peroxide, because of their poisonous nature.

OZONE

In 1785 Van Marum noticed that the atmosphere in the neighbourhood of an electrical generator possessed a fresh penetrating odour, resembling that of very dilute chlorine. Schönbein subsequently (1840) showed that the odour was due to a new substance which he called ozone.

Just as hydrogen peroxide is produced in small quantities whenever atomic hydrogen is liberated in the presence of oxygen, so also is ozone produced in small quantities when atomic oxygen is liberated in the presence of oxygen—

$$H + O_2 + H \rightarrow (H—O—O—H) \text{ or } H_2O_2$$

$$O + O_2 \rightarrow (O \leftarrow O = O) \text{ or } \underset{\text{ozone}}{O_3}$$

Thus small quantities of ozone are formed when oxygen is exposed to ultra-violet radiation, as in the upper atmosphere. It is also formed in the electrolysis of acidulated water, for example, during the electrolysis of dilute sulphuric acid, particularly if the current density at the platinum anode is increased by restricting the size of the platinum. It is formed in many chemical reactions, such as the slow oxidation of white phosphorus, the reaction of fluorine on water (when the liberated oxygen may contain up to 14 per cent of ozone), and in the slow oxidation of many essential

oils in the presence of air and moisture. The "Sanitas" group of disinfectants owe their effectiveness to the formation of ozone as the essential oils present slowly oxidize in air.

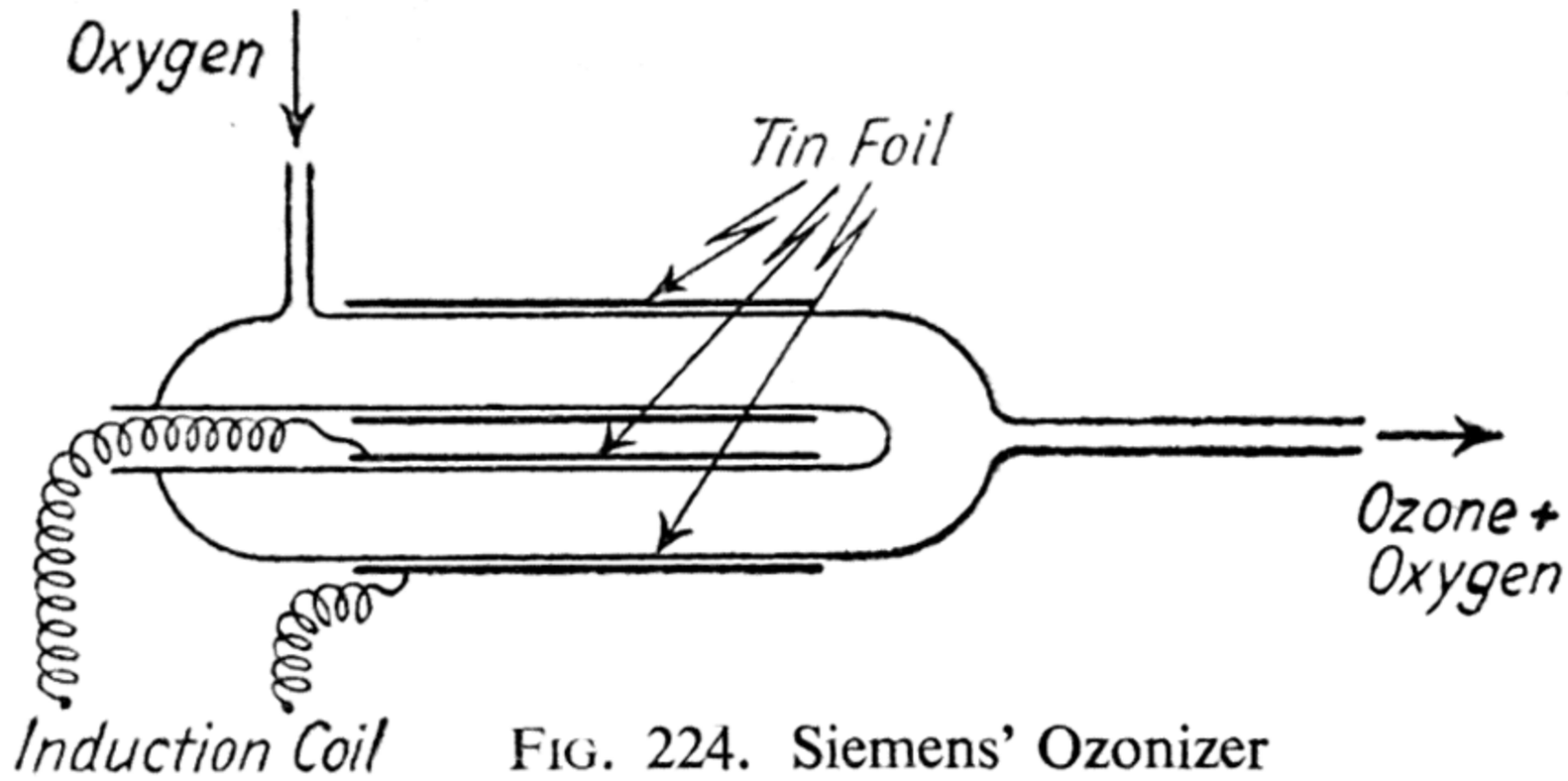


FIG. 224. Siemens' Ozonizer

Preparation of Ozone. Ozone is most conveniently prepared by the action of a silent electric discharge on dry air or oxygen, the essential reaction being—

$$O_2 + O = O_3$$
atomic

The original *Siemens Ozonizer*, shown in the accompanying diagram, consists of two coaxial glass-tubes through which a current of dry air or oxygen may be passed. The outside of the outer glass-tube and the inside of the inner glass-tube are each coated with tin-foil, which are themselves connected to a suitable induction coil. On passing a silent electric discharge between these two plates, some conversion of the oxygen to ozone occurs, and the issuing gas may contain up to about 8 per cent ozone.

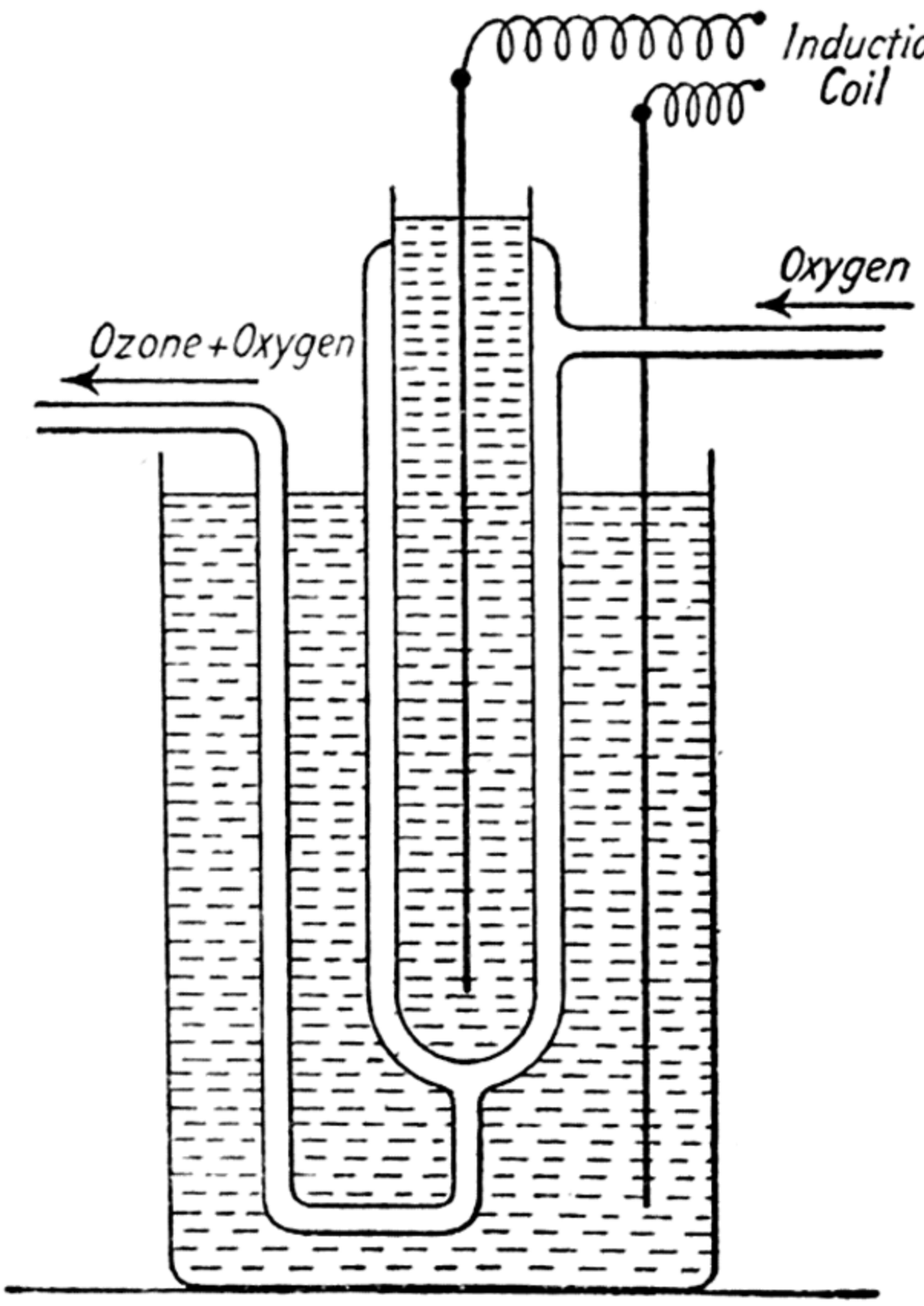


FIG. 225. Brodie Ozonizer

The *Brodie Ozonizer* works on the same principle, except that the two tin-foil plates are replaced by suitable conducting solutions, such as sulphuric acid or aqueous copper sulphate, in which are immersed two suitable electrodes connected to the induction coil.

If the resulting ozonized oxygen is passed through a condenser cooled

in liquid oxygen, a solution of ozone in liquid oxygen is produced, and from this deep-blue liquid, ozone may be obtained on evaporating off the oxygen.

Properties of Ozone. Ozonized air or oxygen has an unpleasant penetrating smell, reminiscent of dilute chlorine. In very small concentrations it has a refreshing effect when breathed, but higher concentrations cause head-aches and sore throats. It may be obtained, as described above, as a liquid with a deep blue colour, boiling at − 119°C. In the liquid state, it is said to be explosive, although in the complete absence of dust or organic matter it may be vaporized without appreciable decomposition. It is rather more soluble than oxygen in water to which it imparts a disagreeable taste and smell. When used to sterilize drinking water, a practice adopted for example in some parts of France, it is therefore necessary to aerate the water to make it palatable again.

Decomposition. The reaction—

$$3O_2 \rightleftharpoons 2O_3 - 68\,000 \text{ cal.}$$

is reversible and strongly endothermic. Considerations of Le Chatelier's Principle suggests that the equilibrium yield of ozone may be increased by increase of pressure and by increase of temperature. Thus, the equilibrium proportion of ozone increases from 0·1 per cent at 2 200°C to about 1 per cent at 3 200°C, and still higher proportions would be produced at higher temperatures. In the methods for preparing ozone described above, the proportion of ozone produced at ordinary temperatures is considerably higher than these equilibrium values suggest. This apparent anomaly is due to the fact that the ozone is in these cases prepared, not by the reaction of oxygen molecules with themselves, but rather by the reaction of oxygen molecules with oxygen atoms, the latter being produced by the silent electric discharge or other process.

$$O_2 + O = O_3$$

The resulting ozone then tends to decompose in accordance with the equilibrium—

$$2O_3 \rightleftharpoons 3O_2$$

until the equilibrium concentration pertaining to the particular temperature conditions is reached. At ordinary temperatures this concentration is negligible. That the ozone does not decompose rapidly at ordinary temperatures, however, is due to the effect of temperature on the time required to reach the above equilibrium state. As a general rule it may be stated that increasing the temperature by about 10°C approximately doubles the speed of a gaseous reaction, and since this rule applies to both the forward and reverse reactions involved in the above equilibrium, such a temperature increase has the effect of halving the time to reach equilibrium.

Conversely, reducing the temperature by about 10°C approximately doubles the time to reach equilibrium, so that although ozone decomposes rapidly at about 300°C, at 0°C the time required would be approximately 2^{30} (that is, about 1 000 000 000) times as long. It follows, therefore, that in the electrical discharge method for producing ozone the temperature should be kept as low as possible to prevent too rapid a decomposition of the ozone. Commercial ozonizers are therefore air or water cooled.

The rapid decomposition of ozone which occurs in the presence of certain substances is explained as follows.

The rate of a reaction may also be considerably increased by increasing the temperature and also by the action of a catalyst. A catalyst is a substance which speeds up the rate of a reaction without itself being chemically changed at the end of the reaction. In the case of a reversible reaction, the rates of both the forward and reverse processes are increased by the same amount so that the position of equilibrium remains the same as it would be in the absence of the catalyst. It has been stated, however, that the percentage of ozone *in equilibrium* with oxygen at ordinary temperatures is negligible, and this explains why some substances can very rapidly decompose ozone at ordinary temperatures. They so speed up the rates of the forward and reverse reactions, that the equilibrium is produced very rapidly and the ozone is said to have been catalytically decomposed. Decomposition catalysts for ozone include finely divided metals, such as platinum, silver and palladium, various metallic oxides, such as those of manganese, iron, silver and lead, and most forms of dust including finely powdered glass.

With metallic silver and mercury, the decomposition probably involves the intermediate formation of the metallic oxide. Thus, when a globule of mercury is exposed to ozonized oxygen, it loses its lustre and wets the glass with a film which consists probably of very finely divided mercury.

$$Hg + O_3 = HgO + O_2\uparrow$$

$$HgO + O_3 = Hg + 2O_2\uparrow$$

This "tailing" of mercury is destroyed by shaking with water, and the original lustre restored. If a piece of freshly cleaned silver foil be heated in the bunsen flame before exposure to ozonized oxygen, it rapidly darkens, possibly due to the formation of an unstable silver oxide or peroxide which decomposes to form a very finely divided deposit of silver metal.

Oxidizing Properties of Ozone. Ozone is a powerful oxidizing agent, although its reactivity is of course limited by its existence only in relatively low concentrations. It liberates iodine from potassium iodide solutions (moistened starch-iodide paper is quickly turned blue)—

$$2KI + H_2O + O_3 = 2KOH + O_2\uparrow + I_2$$

oxidizes several metallic sulphides to sulphates—

$$PbS + 4O_3 = PbSO_4 + 4O_2 \uparrow$$

and converts ferrous salts to ferric salts and ferrocyanides to ferricyanides—

$$2FeSO_4 + H_2SO_4 + O_3 = Fe_2(SO_4)_3 + O_2 \uparrow + H_2O$$
$$2K_4[Fe(CN)_6] + H_2O + O_3 = 2K_3[Fe(CN)_6] + 2KOH + O_2 \uparrow$$

In these reactions it will be noted that the ozone behaves as if it were a carrier of atomic oxygen, as suggested by liberation of oxygen gas—

$$O_3 = O_2 + \overline{\overline{O}}$$

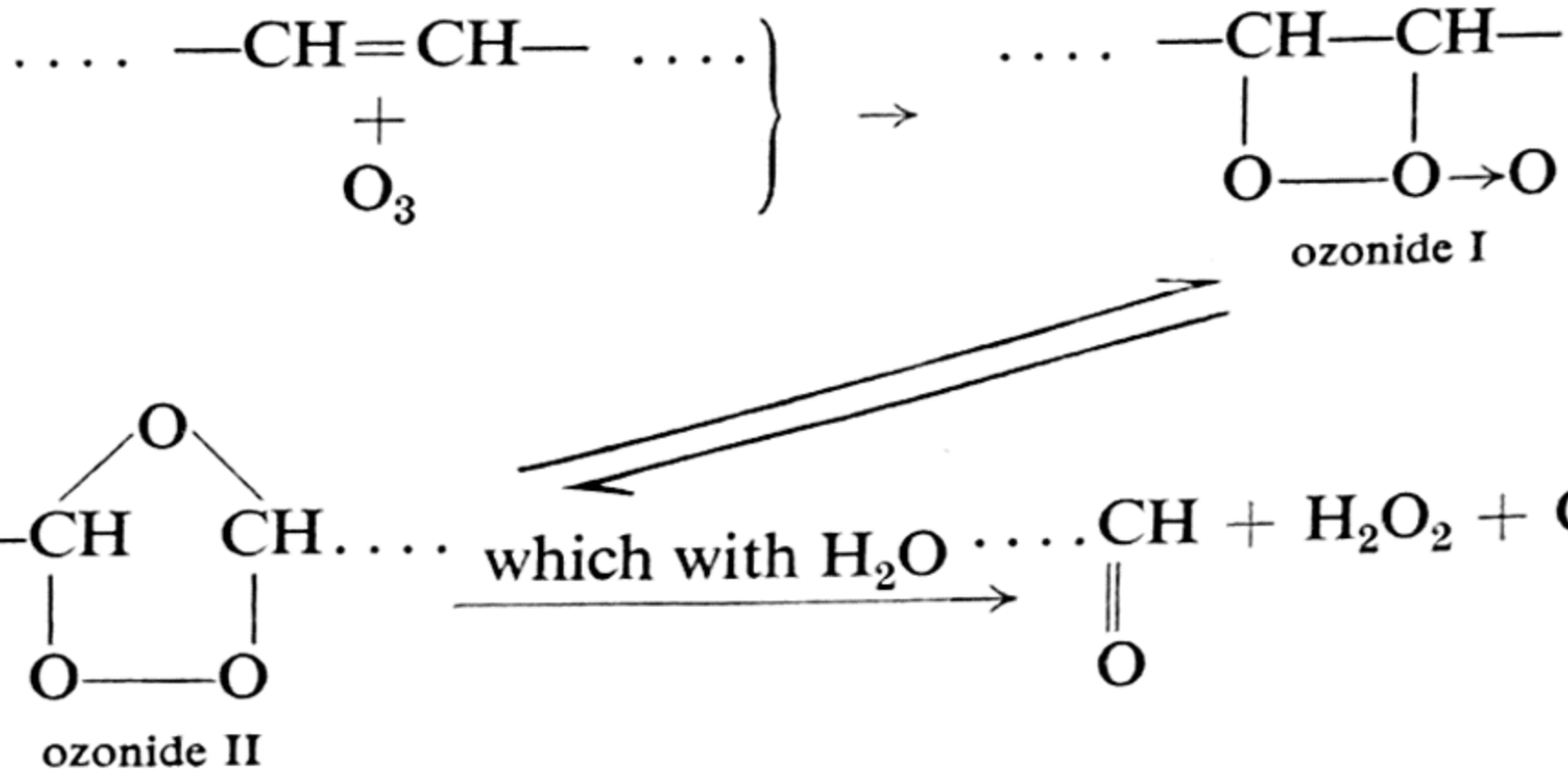
Although ozone reacts in the same way with peroxides, such as hydrogen and barium peroxides, it does not (contrast hydrogen peroxide) react with chromic acid nor with potassium permanganate.

$$BaO_2 + O_3 = BaO + 2O_2 \uparrow$$
$$H_2O_2 + O_3 = H_2O + 2O_2 \uparrow$$

In some of its reactions, however, the whole of the ozone molecule is absorbed and no oxygen is evolved. Examples of this type of reactivity are shown with sulphur dioxide and with stannous chloride—

$$3SO_2 + O_3 = 3SO_3$$
$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O$$

and also with many unsaturated organic compounds (*see* p. 872 for discussion of *unsaturation* as applied to organic compounds). In the latter reactions, the molecule of ozone adds on directly at the double-bond to form a class of compounds which are known as *ozonides*. These are decomposed by water to form hydrogen peroxide.



The solution of ozone in turpentine, cinnamon oil, benzene, etc., are all reactions of this type. The reaction is often used as a test of unsaturation in an organic compound.

Formula of Ozone. The determination of the formula of ozone may be divided into two parts—

(*a*) to show that oxygen is the only element involved, and
(*b*) to show that the formula is O_3.

That ozone contains only oxygen was established by several investigators, and particularly by Andrews and Tait in 1860, and by Soret in 1863. The former investigators observed the contraction in volume which took place when pure dry oxygen was exposed to a silent electric discharge in a closed tube provided with a mercury manometer. A maximum contraction of one-twelfth was noted. On heating the tube to about 300°C (to destroy the ozone) and again cooling to room temperature, the volume was restored to its original value. The experiment was then repeated up to the stage of observing the contraction after passing the silent electric discharge, and then a small sealed tube containing potassium iodide solution was broken inside the main tube. Iodine was produced without further change in volume. That the iodine was produced by reaction with the ozone was then shown by repeating the heating to 300°C. No increase in volume occurred, showing that the whole of the ozone had been destroyed by reaction with the potassium iodide, and it was concluded therefore that ozone is a form of oxygen. This conclusion was confirmed by Soret in 1863.

Odling suggested that the reason why no change in volume resulted on adding the potassium iodide in Andrews and Tait's experiment was due to the reaction—

$$2KI + O_3\,(1\text{ volume}) + H_2O = 2KOH + O_2\,(1\text{volume}) + I_2$$

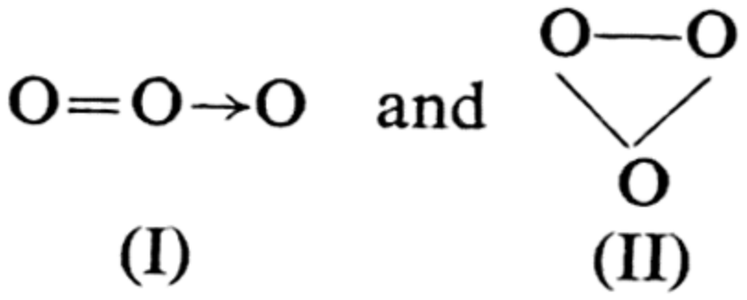
in which ozone has the formula O_3. It was left to Soret in 1866, however, to establish that the formula is actually O_3. He took two equal samples of the *same specimen* of ozonized oxygen in two suitably graduated glass tubes, as shown in the diagrams (Fig. 226). Since any mixture of gases must be uniform in composition, it followed that each of his samples of ozonized oxygen contained the same volume of ozone. He determined this volume of ozone by introducing a small quantity of turpentine or cinnamon oil into one of the tubes, the change in volume being equal to the volume of ozone present. The second tube was then heated to about 300°C (to decompose the ozone), and on cooling it was found that the volume increase was equal to one-half of the contraction in the first tube. It therefore followed, as shown in the diagrams, that two volumes of ozone produce three volumes of oxygen, whence, by Avogadro's hypothesis—

$$2 \text{ molecules of ozone} \rightarrow 3 \text{ molecules of oxygen}$$

$$2O_x = 3O_2$$

and the formula of ozone is "O_3"

Strictly speaking, therefore, ozone is a polymer of oxygen. Two structures have been suggested—



(I) (II)

The evidence favours the first of these two formulae. Thus the infra-red

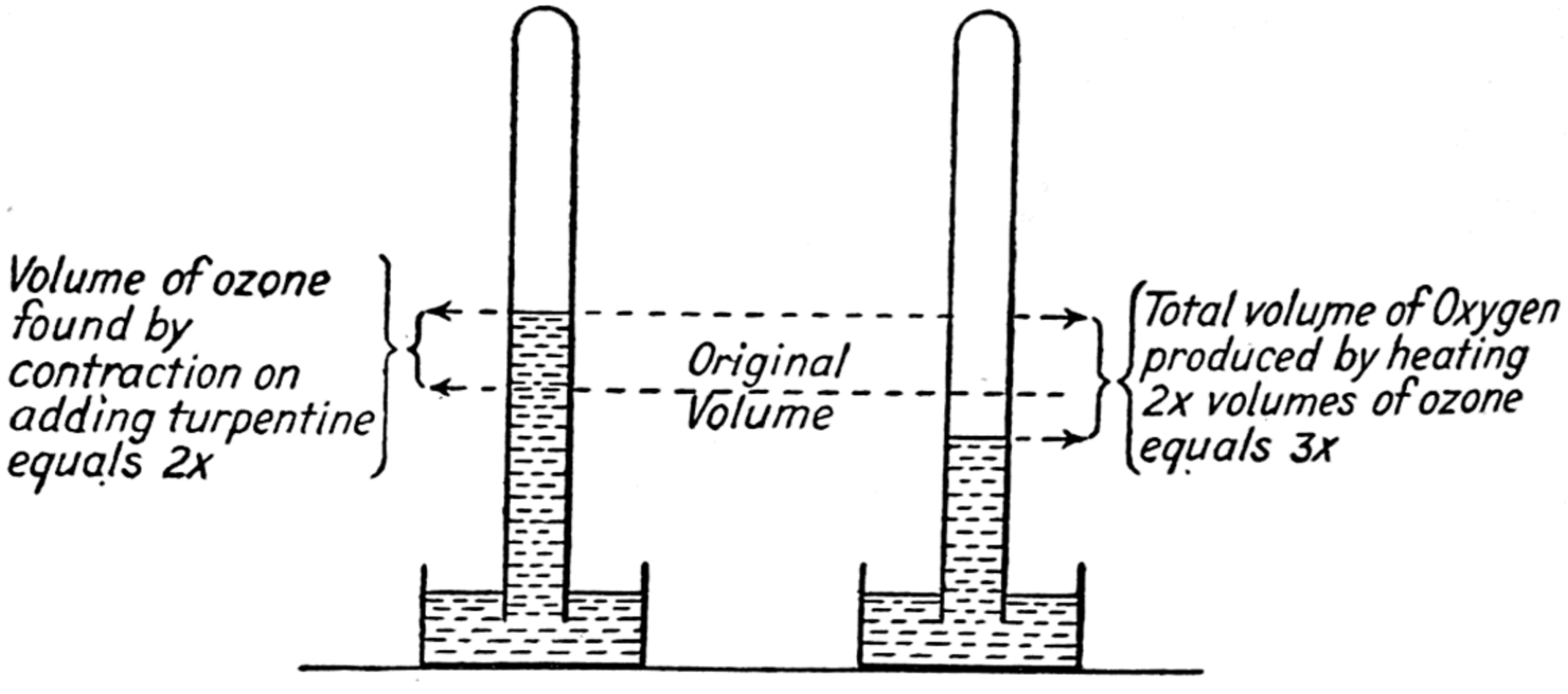
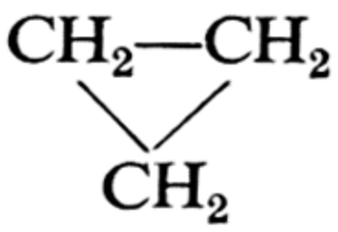
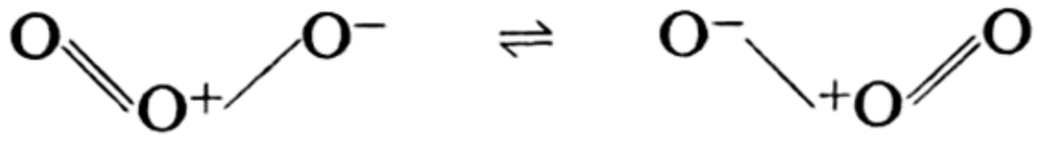


FIG. 226. Formula of Ozone

spectrum of ozone has nothing in common with that of cyclo-propane



but does resemble those of nitrogen peroxide and nitrosyl chloride, NOCl. The molecule is not however straight as suggested by formula I. since electron diffraction measurements have shown the angle between the three oxygen atoms to be about 127°. Ozone is therefore considered to be a resonance hybrid of the two forms—



Detection and Estimation of Ozone. The reaction of ozone with starch-iodide paper is not specific for ozone. The halogens, hydrogen peroxide, and some oxides of nitrogen (N_2O_3, NO_2 and N_2O_4) also liberate iodide from potassium iodide.

Test-papers soaked in an alcoholic solution of *tetramethyl base* (tetra-methyl-diamino-diphenylmethane) are turned violet by ozone, deep blue by chlorine or bromine, and straw-yellow by oxides of nitrogen; hydrogen peroxide has no action.

Ozone may be distinguished from hydrogen peroxide vapour by the fact that the latter decolorizes acidified potassium permanganate, and also forms the blue *perchromic acid* with acidified potassium dichromate.

Ozone may be estimated by passing the gas through a *neutral* solution of potassium iodide, and titrating the liberated iodine after slight acidification with a standard solution of sodium thiosulphate using starch indicator.

Uses of Ozone. Ozonized air is sometimes used in the treatment of potable water supplies for the purpose of sterilizing the water and oxidizing organic matter. It is also used to purify air in confined spaces, and is for example used for this purpose in the London Underground railways. It has been used for bleaching paper-pulp, ivory and flour, and in the manufacture of linoleum from linseed oil.

SULPHUR

Occurrence. Sulphur occurs extensively in nature, both in the free (or native) form and also in the combined state. The native deposits are mainly found in the porous limestone deposits of Texas and Louisiana, and also in the volcanic regions of Sicily. Of the many forms in which combined sulphur occurs in nature, mention may be made of the mineral *sulphides*, such as Galena, PbS, Iron Pyrites, FeS_2, Zinc Blende, ZnS, and Cinnabar, HgS, and also of the *sulphates*, such as Gypsum, $CaSO_4 . 2H_2O$, Barytes, $BaSO_4$, Epsom Salts, $MgSO_4 . 7H_2O$.

Extraction. The following are the principal present-day processes—

(*a*) From the natural deposits in Texas and Louisiana by the Frasch Process.

(*b*) From the volcanic deposits in Sicily by the Sicilian Process.

(*c*) From industrial gases containing sulphur dioxide produced in the roasting or smelting of sulphide ores, e.g. zinc blende.

(*d*) From fuel gases, by conversion of the sulphuretted hydrogen into free sulphur.

Frasch Process. Some 90 per cent of the world's supply of free sulphur is now obtained from the Texas and Louisiana deposits by this process. The sulphur occurs in sulphur-bearing porous limestone formations which occur from 500 to 1500 ft below the surface. The obvious process of mining the ore proved impracticable due to the difficulties of sinking shafts through water-logged sands, clay and rock strata, and by the considerable amounts of sulphur dioxide and sulphuretted hydrogen gases which were encountered. The problem of how to recover the sulphur was eventually solved towards the end of the last century by Hermann Frasch, who conceived the idea of melting the sulphur by forcing superheated water into the sulphur-bearing strata and then pumping the liquid sulphur to the surface.

Ordinary oil-well equipment is used to bore holes to the bottom of the sulphur-bearing strata, and a "nest" of three (or four) concentric pipes,

varying in size from 6 in. to 1 in. diameter then inserted as shown in the accompanying diagram. The outside pipe passes through the sulphur-containing limestone, and rests on the upper portion of the solid anhydrite ($CaSO_4$) rock. A 3-in. pipe passes inside the 6-in. pipe and rests on a collar which seals the annular space between the 6-in. and 3-in. pipes. An air-pipe, 1 in. in diameter and concentric with the others, opens into the space above this collar. The 6-in. pipe is perforated at two different levels, one immediately above and the other below the annular collar.

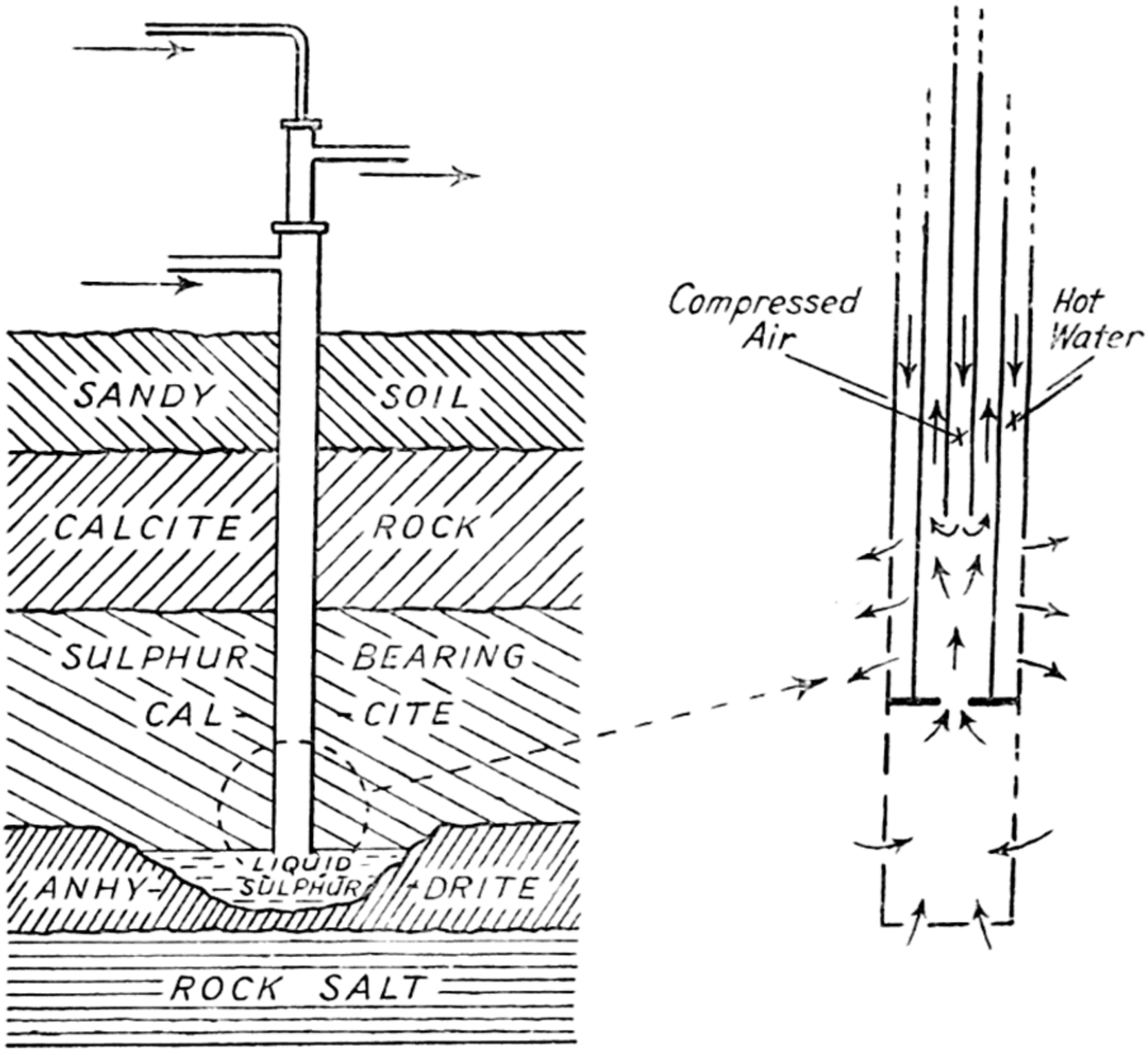


FIG. 227. Frasch Process

Superheated water at about 165°C under a pressure of 10–18 atmospheres is forced down the outer annular pipe (or outer two pipes, if a nest of four concentric pipes be used) and discharges through the upper perforations into the porous formation near the foot of the well. The sulphur is thereby melted and collects as a liquid around the base of the well. It enters the pipes through the lower perforations and rises in the space between the 3-in. and 1-in. pipes. Air compressed to about 35 atmospheres pressure is then forced down the inner pipe and mixes with the liquid sulphur to form an aerated sulphur-water emulsion which rises to the surface. The outer superheated water jacket, in the space between the 6-in. and 3-in. pipes, not only supplies the heat for melting the sulphur, but also the heat necessary to keep this ascending emulsion fluid on its way to the surface.

At the surface, the sulphur is collected in steam-heated pans, and then pumped through pipes, heated by an inner steam-pipe, into large storage vats where the sulphur solidifies to produce blocks of 99·5 per cent pure sulphur, often up to a quarter of a mile long and over 50 ft in height. New sulphur wells are started as the old ones become dry, so that the industry is essentially an intermittent one, in which the accumulation of large stocks ensures a continuous supply in spite of delays in locating new wells, delays which may last as long as six months.

The sulphur so produced is extremely pure, 99·5 per cent or more and requires no further purification.

Sicilian Process. For a long time the only source of free sulphur, this process has now very largely been eclipsed by the Frasch Process. The volcanic rock, containing up to 25 per cent of free sulphur is stacked in brick kilns, known as "calcaroni," built on sloping hill-sides. Air-holes are provided during the stacking, and a covering of powdered ore completes the assembly. The kiln is lighted at the top, and the heat liberated by the burning sulphur melts the remainder which collects at the lowest point of the kiln. The kilns are periodically tapped and the sulphur allowed to run out and solidify in wooden moulds. The sulphur so obtained is far from pure and has to be purified by distillation, a process which, owing to the absence of coal in Sicily, is more economically effected by exporting the crude sulphur to Marseilles, where it is refined.

The considerable wastage of sulphur in the old calcaroni method has led to various modifications with the object of utilizing to the full the heat liberated by the burning sulphur. In the Gill modification, six closed brick chambers are arranged in a circle, and are so connected that the hot gases from one kiln pass into the next and so on. The otherwise waste heat is thus used to heat up fresh rock, and the yield of sulphur is thereby increased.

The purification of the impure sulphur is carried out by distillation. The sulphur vapour is condensed in large brick-work chambers. At first, when the walls are cold, the sulphur condenses as the familiar *flowers of sulphur* (and may be removed), but later, as the brick-work heats up to above 120°C, the condensate remains liquid and collects on the floor of the chambers, from which it is periodically tapped and allowed to run into moulds to form *roll-sulphur* or brimstone.

Sulphur Dioxide Process. On roasting sulphide ores, such as lead, zinc, copper and iron sulphides in the recovery of these metals, considerable quantities of sulphur dioxide gas are evolved. Some of this gas is used directly in the manufacture of sulphuric acid, but much which was formerly allowed to escape into the atmosphere is now treated to recover the sulphur, and constitutes a very important source of this element, particularly in those countries which do not possess natural deposits of free sulphur. The recovery process may be considered in two stages; first, concentration of

the sulphur dioxide to practically 100 per cent SO_2, which, in the second stage, is then converted into free sulphur.

(*a*) *Concentration of the Sulphur Dioxide*—

(i) At Billingham, a solution of basic aluminium sulphate is treated with sulphur dioxide to produce a sulphite-bisulphite solution which possesses the property of dissolving more SO_2 in the cold and liberating it later when the solution is heated.

(ii) Alternatively, the furnace gases are passed into a solution of ammonium sulphite to form ammonium bisulphite, and this, when subsequently treated with concentrated sulphuric acid, liberates a 100 per cent sulphur dioxide.

$$(NH_4)_2SO_3 + SO_2 + H_2O = 2NH_4HSO_3$$

$$2NH_4HSO_3 + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O + 2SO_2\uparrow$$

(*b*) *Sulphur from Concentrated Sulphur Dioxide.* The sulphur dioxide is passed through a bed of white-hot coke at a temperature of about 1000–1100°C—

$$SO_2 + C = CO_2 + S$$

The reaction is exothermic, so that once this temperature is reached, no further external heating is required. The sulphur distils over and is condensed to produce 99·99 per cent commercial brimstone.

Sulphuretted Hydrogen Process. Most gaseous fuels (coal-gas, water-gas, producer-gas, etc.) contain more or less sulphuretted hydrogen. Thus, coal gas may contain up to 2 per cent H_2S as it leaves the retorts. This sulphuretted hydrogen is removed in most gas works by passing the gas through a series of boxes containing hydrated iron oxide—

$$Fe_2O_3 \,.\, xH_2O + 3H_2S = Fe_2S_3 + (3 + x)H_2O$$

The ferric sulphide may be converted back to the hydrated oxide by moistening and exposure to the air—

$$2Fe_2S_3 + 3O_2 + 2xH_2O = 6S + 2Fe_2O_3 \,.\, xH_2O$$

More usually, by the regulated introduction of about 2 per cent of air into the gas *before* passing over the iron oxide, the ferric sulphide first formed is converted back to ferric oxide with separation of free sulphur. Eventually, a product containing as much as 60 per cent of free sulphur is obtained. This *spent oxide* is mostly used at the gas-works as a source of sulphur dioxide for the manufacture of sulphuric acid, but in Germany the sulphur is extracted by carbon disulphide and subsequently recovered pure.

Other methods for removing sulphuretted hydrogen from fuel gases and recovering the sulphur include the Thylox Process in which an aqueous

solution of arsenious oxide in sodium carbonate dissolves the sulphuretted hydrogen, and the solution on subsequent aeration deposits free sulphur. The reactions are complex, but are mostly simply represented by—

$$Na_4As_2S_5O_2 + H_2S = Na_4As_2S_6O + H_2O$$
$$2Na_4As_2S_6O + O_2 = 2Na_4As_2S_5O_2 + S$$

In the Ferrox Process a suspension of ferric hydroxide in a dilute solution of sodium carbonate is used to absorb the sulphuretted hydrogen. On aeration, the sulphur separates and may be floated off to leave the original solution. The net reaction may be depicted—

$$2H_2S + O_2 = 2H_2O + 2S$$

The Chance-Claus Process for the recovery of sulphur from the alkali-wastes of the now obsolete Leblanc Soda-Process is interesting although not of much practical importance to-day. Treatment of the alkali-waste (made into a sludge with water) with carbon dioxide converts the calcium sulphide first into calcium hydrogen sulphide and then into calcium carbonate with liberation of sulphuretted hydrogen—

$$2CaS + CO_2 + H_2O = CaCO_3 + Ca(HS)_2$$
$$Ca(HS)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S\uparrow$$

The sulphuretted hydrogen is then mixed with an appropriate amount of air and burnt in a Claus Kiln containing ferric oxide which catalyzes the reaction—

$$2H_2S + O_2 = 2H_2O + 2S$$

Uses of Sulphur. The most extensive use of sulphur is in the manufacture of sulphuric acid, but considerable quantities are used in the manufacture of explosives (gunpowder, propellents, pyrotechnics), in the vulcanizing of rubber, in the manufacture of matches, of sodium bisulphite used in paper manufacture, in the fine-dust form or as polysulphides as contact insecticides, and also for dusting sand-moulds in the manufacture of magnesium alloy castings.

Physical Properties of Sulphur. The properties of sulphur are largely determined by the form in which it is obtained. Flowers of Sulphur and Roll Sulphur are familiar commercial varieties, produced in the purification of the crude sulphur, and must not be confused with the pure allotropic varieties, such as rhombic and monoclinic described below. In general, sulphur may be described as a pale yellow solid, which boils at 444·6°C. Its melting point is less definite, and may vary from 112·8°C in the case of rhombic sulphur to 119·25°C in the case of monoclinic sulphur. All varieties are insoluble in water, and only the crystalline forms are soluble in carbon disulphide and sulphur monochloride (S_2Cl_2) liquids. Exceptions to these general remarks will be further discussed in connexion with the allotropy of sulphur.

The Allotropy of Sulphur

The existence of an element in more than one physical form is termed *allotropy*, and we speak of the allotropic forms of that element. Thus, diamond and graphite are allotropic forms of the element carbon, whilst the allotropic varieties of phosphorus include red, white and black phosphorus. The term allotropy is sometimes however applied in a wider sense to include compounds which occur in different crystalline forms, but modern practice inclines to the use of the term *polymorphism* in such cases. Thus we speak usually of the polymorphism of mercuric iodide, or of ammonium nitrate, etc., rather than of their allotropy.

Three types of allotropy are recognized; namely, enantiotropic, monotropic, and dynamic allotropy. Examples of all three occur in the allotropy of sulphur and will be discussed as they arise. Sulphur occurs in four different crystalline forms, namely, rhombic, monoclinic, nacreous and tabular sulphur.

Rhombic Sulphur (known also as α-sulphur, or rhombohedral sulphur) is the stable form of sulphur at ordinary temperatures. It is prepared by allowing a solution of sulphur in carbon disulphide to crystallize by evaporation. The small yellow rhombic crystals obtained melt at 112·8°C if heated quickly, but if heated slowly then at 96°C a change to the second allotropic form, monoclinic sulphur, tends to occur, the melting point of which is at 119°C. Below 96°C, the change is reversed, and monoclinic sulphur tends to change to rhombic sulphur, thus—

$$\text{Rhombic sulphur} \rightleftharpoons^{96^\circ\text{C}} \text{Monoclinic sulphur}$$

Only at 96°C are both forms equally stable; above this temperature monoclinic sulphur is stable and rhombic sulphur is unstable, but below this temperature the stabilities are reversed. 96°C is accordingly known as the transition temperature for the change rhombic ←→ monoclinic sulphur.

Consider the vapour pressure diagram of sulphur (Fig. 228). Since the form having the lower vapour pressure is always the more stable form, the change in the relative stability of the two forms in passing through 96°C is clearly due to the two vapour pressure curves intersecting at this temperature. This type of allotropy in which the two vapour pressure curves intersect below the melting point of both forms is known as *Enantiotropic Allotropy*, and implies the existence of a definite transition temperature at which a change in the solid state occurs.

Monoclinic sulphur (known also as β-sulphur, or prismatic sulphur). Since monoclinic sulphur is only stable between the temperatures of 96°C and 119°C (its melting point), it follows that it can only be prepared between these limits. The usual method is to allow molten sulphur to cool *slowly*, for example, in a large evaporating basin. As soon as a solid crust forms,

it is pierced by two small holes, diametrically opposite, through one of which any remaining liquid sulphur is quickly poured off. The crust is then removed to reveal long needle-like crystals of monoclinic sulphur.

Nacreous and Tabular Sulphur are two further crystalline forms of sulphur, which are both somewhat difficult to prepare. They are unstable at all temperatures and slowly revert to the rhombic or monoclinic forms depending on whether the temperature is below or above 96°C. Nacreous sulphur is deposited in pearly crystals when a solution of sulphur in benzene or turpentine is rapidly cooled. Both are monotropic allotropes of sulphur, but the student is referred to the allotropy of phosphorus and to p. 162 for a fuller discussion of monotropic allotropy.

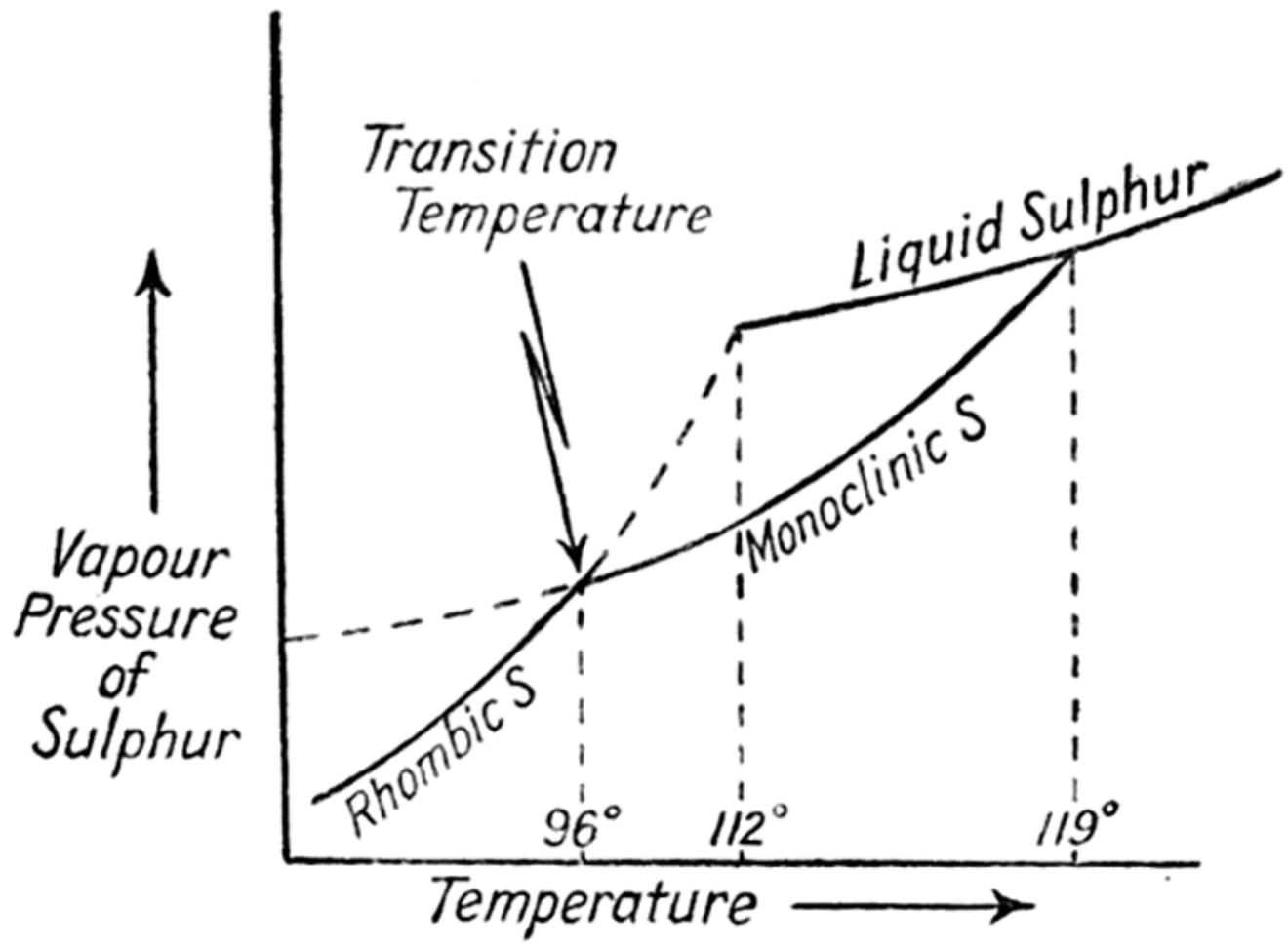


FIG. 228. Vapour Pressure—Temperature Diagram for Rhombic and Monoclinic Sulphur

Behaviour of Sulphur on Heating. When heated slowly, sulphur first melts to a pale-yellow liquid. As the temperature of this liquid is increased two changes appear to occur. The colour reddens and ultimately becomes so dark as to appear almost black at the boiling point, 444·6°C. This colour change is accompanied by an unexpected change in viscosity which has only been satisfactorily explained in recent times. The liquid sulphur increases in viscosity until at about 180°C it is so viscous that it cannot be poured. With further increase in temperature, the viscosity again slowly decreases, so that near the boiling point the sulphur behaves as a normal mobile liquid.

The original explanation of this behaviour assumes the existence of three liquid allotropic varieties of sulphur, known as λ-sulphur (lambda), μ-sulphur (mu), and π-sulphur (pi). Liquid sulphur near the melting point was considered to be mainly λ-sulphur. With increase in temperature, the proportion of μ-sulphur in equilibrium with the λ-sulphur increased and the solution became increasingly viscous. The later decrease in

viscosity with further increase in temperature then resulted from a progressive increase in the third variety, namely, π-sulphur. Thus *Plastic Sulphur*, produced by *rapidly* cooling molten sulphur from a temperature near the boiling point, for example, by pouring into water, was considered to consist mainly of π-sulphur.

This behaviour in which two or more different allotropic forms may exist together in stable equilibrium over a range of temperatures, the proportions only varying with change in temperature, is known as *Dynamic Allotropy*.

The modern explanation of the behaviour of sulphur on heating is based on the evidence of X-ray crystal structure analysis. Both rhombic and monoclinic sulphur have the molecular formula S_8, in which the eight atoms are arranged in the form of a puckered ring, thus—

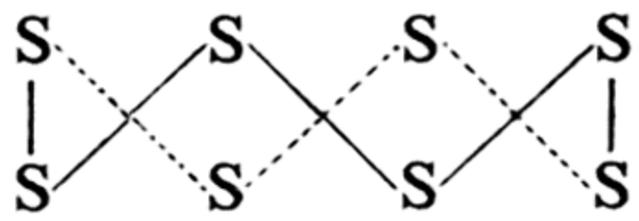
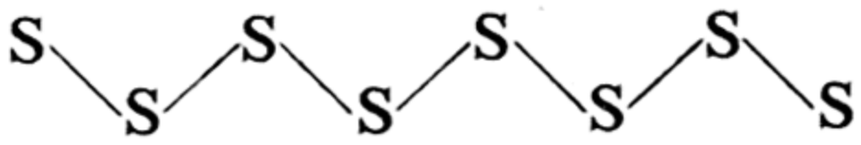


FIG. 229. S_8 Molecule (*see* page 71)

These rings remain unbroken when sulphur is first melted, but with increase in temperature and hence increase in vibrational energy, the rings open to form long zig-zag chains of sulphur atoms, thus—



The increase in viscosity is attributed to the entanglement of these chains with other similar chains. With further increase in temperature, these chains tend to disintegrate until at the boiling point, the molecular formula is mainly S_2. This progressive disintegration is accompanied, as might be expected, by a decrease in viscosity. If sulphur near the boiling point be rapidly cooled, the eight-membered rings of rhombic and monoclinic sulphur do not have time to form, and although association of the S_2 molecules to form S_4, S_6 and S_8 chains occurs, these will be mainly in an intertwined random state, and the resulting solid sulphur is *plastic*. The eventual change of plastic sulphur to rhombic sulphur is due to these chains sorting themselves out and reforming the eight-membered ring structures. Plastic sulphur is thus a rubbery solid, due to its entangled structure, and is insoluble in carbon disulphide.

Amorphous Sulphur. When sulphur is suddenly precipitated from solution as the result of a chemical reaction, it assumes a non-crystalline (amorphous) finely divided form. Sometimes the particles of sulphur are so finely divided that they form a colloidal solution, which cannot be separated by simple filtration. Such is the case when an alcoholic solution of sulphur is poured into water, when a solution of sodium thiosulphate

is acidified, or when sulphuretted hydrogen is passed into a saturated solution of sulphur dioxide—

$$\underset{\text{thiosulphate}}{Na_2S_2O_3} + 2HCl = 2NaCl + SO_2\uparrow + H_2O + S\downarrow$$

$$2H_2S + SO_2 = 2H_2O + 3S\downarrow$$

When a solution of sodium or ammonium polysulphide is acidified, then, particularly if the solution is dilute, the particles of sulphur are so small that the resulting *solution*, known as *milk of sulphur* appears to be almost white in colour.

$$Na_2S_5 + 2HCl = 2NaCl + H_2S + 4S$$

Chemical Properties of Sulphur. Sulphur combines directly with most metals on heating to form the sulphides, for example, Cu_2S, Ag_2S, FeS, SnS, etc. A mixture of iron powder and sulphur when heated to initiate the reaction becomes incandescent due to the exothermic nature of the reaction—

$$Fe + S = FeS$$

The resulting compound ferrous sulphide is used extensively in most laboratories to generate sulphuretted hydrogen.

Sulphur burns in air with a very pale blue flame, or in oxygen with a bright blue flame (due to the more intense reaction) to form sulphur dioxide and a little sulphur trioxide gases.

Sulphur also unites directly on heating with other non-metals, such as the halogens, phosphorus, carbon and hydrogen. The reactivity with the halogens decreases in the order, fluorine to iodine. Fluorine forms the very stable sulphur hexafluoride SF_6, chlorine the less stable sulphur monochloride S_2Cl_2 which unlike the hexafluoride is hydrolyzed by water—

$$2S_2Cl_2 + 3H_2O = 4HCl + H_2SO_3 + 3S\downarrow$$

Phosphorus forms the pentasulphide P_2S_5 and also tetra-phosphorus tri-sulphide P_4S_3 when heated with sulphur.

The reactions with carbon and hydrogen occur less readily, and in the former case requires a considerable temperature such as that obtained in the electric-furnace to produce carbon disulphide CS_2.

Sulphur is insoluble in dilute acids, but dissolves slowly on heating with concentrated sulphuric acid, more readily with concentrated nitric acid, and is slowly soluble in hot solutions of the alkalis

Hot concentrated H_2SO_4: $S + 2H_2SO_4 = 3SO_2\uparrow + 2H_2O$

Hot concentrated HNO_3: $S + 6HNO_3 = H_2SO_4 + 6NO_2 + 2H_2O$

Hot strong NaOH: Sulphides and thiosulphates formed—

$$6NaOH + 4S = Na_2S_2O_3 + 2Na_2S + 3H_2O$$

followed by solution of sulphur in the sodium sulphide to form sodium pentasulphide—

$$Na_2S + 4S = Na_2S_5$$

Reactions with potassium hydroxide and calcium hydroxide are similar.

The reaction with concentrated nitric acid is the basis of the quantitative method for estimating free sulphur. The sulphur is quantitatively converted into sulphuric acid, which is then precipitated as barium sulphate on adding barium chloride solution. The barium sulphate is collected, dried, and weighed.

Compounds of Sulphur

Sulphuretted Hydrogen or Hydrogen Sulphide, H_2S. The usual laboratory method is to add dilute sulphuric or hydrochloric acid to solid ferrous sulphide, and if the reaction be carried out in a Kipp's apparatus (*see* p. 362) a supply of the gas is always available simply by turning on the tap.

$$FeS + H_2SO_4 = FeSO_4 + H_2S \uparrow$$

The gas, so prepared, usually contains some hydrogen from the iron present as impurity in the ferrous sulphide and also some acid spray. It may be purified from acid spray by bubbling through a saturated solution of sodium hydrogen sulphide (produced by saturating sodium hydroxide with the gas)—

$$NaOH + H_2S = NaHS + H_2O$$
$$2NaHS + H_2SO_4 = Na_2SO_4 + 2H_2S \uparrow$$

from moisture via calcium chloride (concentrated sulphuric acid should not be used since sulphuretted hydrogen is a reducing agent), and from hydrogen by liquefying the sulphuretted hydrogen in a freezing mixture formed by adding solid carbon dioxide to acetone, the hydrogen passing on.

More simply, it may be freed from hydrogen and acid spray by absorption in a solution of sodium hydroxide, and the resulting solution of sodium hydrogen sulphide treated with dilute acid under air-free conditions to reliberate the sulphuretted hydrogen, as indicated in the above equations.

It is more usual to prepare the sulphuretted hydrogen pure either by the action of water on aluminium sulphide—

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S \uparrow$$

or by the action of concentrated hydrochloric acid on antimony sulphide—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S \uparrow$$

Small quantities of sulphuretted hydrogen may conveniently be prepared in the laboratory by boiling a mixture of paraffin wax and free sulphur. The reaction is easily stopped by allowing the mixture to cool.

The reaction between hydrogen and sulphur occurs to a limited extent

when sulphur is boiled in an atmosphere of hydrogen, but almost complete combination occurs when hydrogen and sulphur vapour are passed together over a finely divided nickel catalyst at a temperature of about 450°C—

$$H_2 + S = H_2S$$

The occurrence of sulphuretted hydrogen in industrial fuel gases (coal gas, etc.) has already been described in connexion with the manufacture of sulphur (*see* p. 734).

Physical Properties of Hydrogen Sulphide. Sulphuretted hydrogen is a colourless gas with the characteristic odour of bad eggs (produced from sulphur compounds in the yoke), and may be liquefied at − 61°C. It is poisonous, much more so than is generally believed, and concentrations of about 0·1 per cent are reported to be fatal, if inhaled for any considerable time. *Weak chlorine* may be inhaled as an antidote. It is moderately soluble in water; the resulting solution, H_2S-water, is very slightly acidic. It may however be collected over hot water.

Chemical Properties of Hydrogen Sulphide. Sulphuretted hydrogen burns in air with a blue flame to form sulphur dioxide and water but if the supply of oxygen is limited, for example, by burning the gas in a gas-jar, the oxidation is incomplete and free sulphur is deposited on the walls—

$$2H_2S + 3O_2 = 2H_2O + 2SO_2\uparrow$$
$$2H_2S + O_2 = 2H_2O + 2S$$

Free sulphur is also deposited when sulphuretted hydrogen is passed into solutions of oxidizing agents, such as the halogens, fairly strong or concentrated nitric acid, concentrated sulphuric acid, dichromate, permanganate, ferric salts, hydrogen peroxide, etc., with results as indicated in the following equations—

$$Cl_2 + H_2S = 2HCl + S$$
$$2HNO_3 + 3H_2S = 3S + 2NO\uparrow + 4H_2O$$
$$2HNO_3\ (\text{concentrated}) + H_2S = S + 2NO_2\uparrow + 2H_2O$$
$$Fe_2(SO_4)_3 + H_2S = S + 2FeSO_4 + H_2SO_4$$
$$H_2O_2 + H_2S = S + 2H_2O$$
$$H_2SO_4 + H_2S = S + SO_2\uparrow + 2H_2O$$
$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

The student will find these equations less difficult to balance if he studies the following illustrative example of procedure in terms of the basic equation for the reaction with potassium permanganate—

(*a*) $2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5\overline{O}$

(*b*) $H_2S + O = H_2O + S$

The correct equation is then found by balancing the oxidizing power of the permanganate (as represented by O) against the oxygen requirements of the sulphuretted hydrogen. Thus, multiply equation (*b*) by five, add to equation (*a*) and then eliminate molecules which occur on both sides of the resulting equation—

$$2KMnO_4 + 3H_2SO_4 + 5H_2S + 5\overline{O} = K_2SO_4 + 2MnSO_4 + 8H_2O + 5S + 5\overline{O}$$

whence

$$2KMnO_4 + 3H_2SO_4 + 5H_2S = K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

Sulphuretted hydrogen is thus a *reducing agent*, and this property often causes some trouble in qualitative analysis when the "unknown" solution contains an oxidizing agent. On passing sulphuretted hydrogen to precipitate the Group II sulphides, if an oxidizing agent is present, a very finely divided precipitate of sulphur is formed, often in the very difficult to remove colloidal form. In practice, this sulphur precipitation may be avoided by first passing sulphur dioxide through the solution to reduce the oxidizing agents, and then boiling out the remaining dissolved sulphur dioxide *before* passing in the sulphuretted hydrogen.

$$SO_2 + 2H_2S = 2H_2O + 3S$$

That hydrogen sulphide acts in solution as a *very weak dibasic acid* is indicated by the following reactions—

(*a*) It turns litmus solution slightly pink.

(*b*) It reacts with sodium hydroxide (and other alkalis) to form first the normal sodium sulphide, Na_2S, and then on saturating the sodium hydroxide with the gas, the acid or hydrogen sulphide, NaHS—

$$2NaOH + H_2S = Na_2S + 2H_2O$$
$$Na_2S + H_2S = 2NaHS$$

The normal sulphide may thus be prepared by first saturating a portion of the given sodium hydroxide solution with the gas, and then adding an equal volume of the *same* sodium hydroxide solution—

$$NaHS + NaOH = Na_2S + H_2O$$

The use of sulphuretted hydrogen in qualitative analysis is based on the fact that sulphides of the analytical Group II elements (Cu, Pb, Bi, Sn, etc.) are all insoluble in dilute acid, whereas those of Group IV (Zn, Mn, etc.) are soluble in acid and are only precipitated from neutral or alkaline solutions of their salts.

More precisely, the precipitation of a metallic sulphide is determined by the value of its solubility product (*see* p. 332). If the product of the ionic concentrations of the metallic ion and of the sulphide ion (produced

by ionization of the sulphuretted hydrogen in solution) exceeds the solubility product, then the sulphide is precipitated. Thus, for copper sulphide solution, if—

$$[Cu^{++}] \times [S^{--}] \text{ is greater than } S_{CuS} (= 8{\cdot}5 \times 10^{-45})$$

then copper sulphide will be precipitated. The concentration of the metallic ion will depend upon the concentration of the original solution, but this will have little significance in view of the very considerable changes which may occur in the sulphide ion concentration. The critical factor is thus the sulphide ion concentration, and this is determined by the hydrogen ion concentration of the solution. Thus if the precipitation is carried out in a solution of a strong acid (hydrochloric acid is a strong acid), the dissociation of the sulphuretted hydrogen—

$$H_2S = 2H^+ + S^{--}$$

is very largely repressed due to the very high hydrogen ion concentration and as a result the value of $[S^{--}]$ will be very small. Only those metallic sulphides which have an extremely small solubility product (CuS, HgS, Sb_2S_3, etc.) will be precipitated, and the student may find that the sulphides of lead and particularly cadmium are not precipitated. If, however, the solution is appreciably diluted, the sulphide ion concentration is increased and lead sulphide and cadmium sulphide are now precipitated, since the product of their ionic concentrations now exceeds their respective solubility products.

A further big increase in the sulphide ion concentration occurs when the precipitation is carried out in alkaline solution, for example, in the presence of ammonium hydroxide in Group IV. The sulphides of zinc, manganese, cobalt and nickel are then precipitated. Zinc sulphide may even be precipitated in Group II, if the solution is diluted too much, due to the reduction in the hydrogen ion concentration.

The separation of the Group II sulphides into sub-groups A and B is based on the solubility of the sulphides of tin, arsenic and antimony in yellow ammonium sulphide to form thio-salts. Free sulphur, present in the yellow ammonium sulphide, is necessary to convert stannous sulphide to stannic sulphide before it dissolves. Otherwise, sodium hydroxide could be used, but not a mixture of ammonium sulphide and sodium hydroxide, since mercuric sulphide is soluble in the resulting sodium sulphide. The equations for the reactions of the Group IIB sulphides with yellow ammonium sulphide and with sodium hydroxide are—

Stannic sulphide—

$$3SnS_2 + 6NaOH = Na_2SnO_3 + 2Na_2SnS_3 + 3H_2O$$

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

Stannous sulphide—

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3$$

Arsenious sulphide—

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$$

$$As_2S_3 + 6NaOH = Na_3AsO_3 + Na_3AsS_3 + 3H_2O$$

Antimony sulphide—

$$Sb_2S_3 + 3(NH_4)_2S_2 = 2(NH_4)_3SbS_4 + S\downarrow$$

On subsequent treatment with dilute acid, the sulphides are reprecipitated.

Detection and Determination of Sulphuretted Hydrogen. Sulphuretted hydrogen is readily detected by smell, and by its action on solutions of soluble lead salts. Thus lead acetate paper (a piece of filter paper dipped into lead acetate solution will suffice) is turned brown and then black on exposure to the gas, due to the formation of lead sulphide.

It may be determined in solution by adding excess of standard iodine solution and the residual iodine is then found by titration with standard sodium thiosulphate in the usual way.

$$H_2S + I_2 = 2HI + S$$

Formula. If dry sulphuretted hydrogen is sparked over mercury, or if metallic tin is heated in a measured volume of the gas, then when the temperature again reaches its initial value, it is found that there is no change in volume. Thus—

$$1 \text{ volume } H_xS_y \text{ gives } 1 \text{ volume of } H_2$$

Therefore, by Avogadro's Hypothesis—

$$1 \text{ molecule } H_xS_y \text{ gives } 1 \text{ molecule of } H_2$$

whence

$$x = 2$$

The vapour density of 17 shows the molecular weight to be 34, and hence the formula of the molecule is H_2S.

Hydrogen Persulphides. Although compounds from H_2S to H_2S_9 have been reported, only H_2S, H_2S_2 and H_2S_3 have definitely been established. Hydrogen persulphide and hydrogen trisulphide are produced when a solution of sodium polysulphide Na_2S_5 is poured into dilute hydrochloric acid. A yellow oil is obtained which may be separated by distillation into H_2S_2 and H_2S_3.

Oxides of Sulphur and their Acids

Sulphur Dioxide, SO_2. The usual laboratory method is to heat a mixture of copper turnings and concentrated sulphuric acid. It will be recalled that copper does not liberate hydrogen from any of the acids, and the

explanation of the present reaction is to be found in the fact that sulphuric acid is an oxidizing agent when it is both hot and concentrated. The sequence of reactions is probably—

Oxidation—

$$Cu + H_2SO_4 = CuO + H_2O + SO_2 \uparrow$$

Neutralization—

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

The equation representing the net result is therefore—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2 \uparrow$$

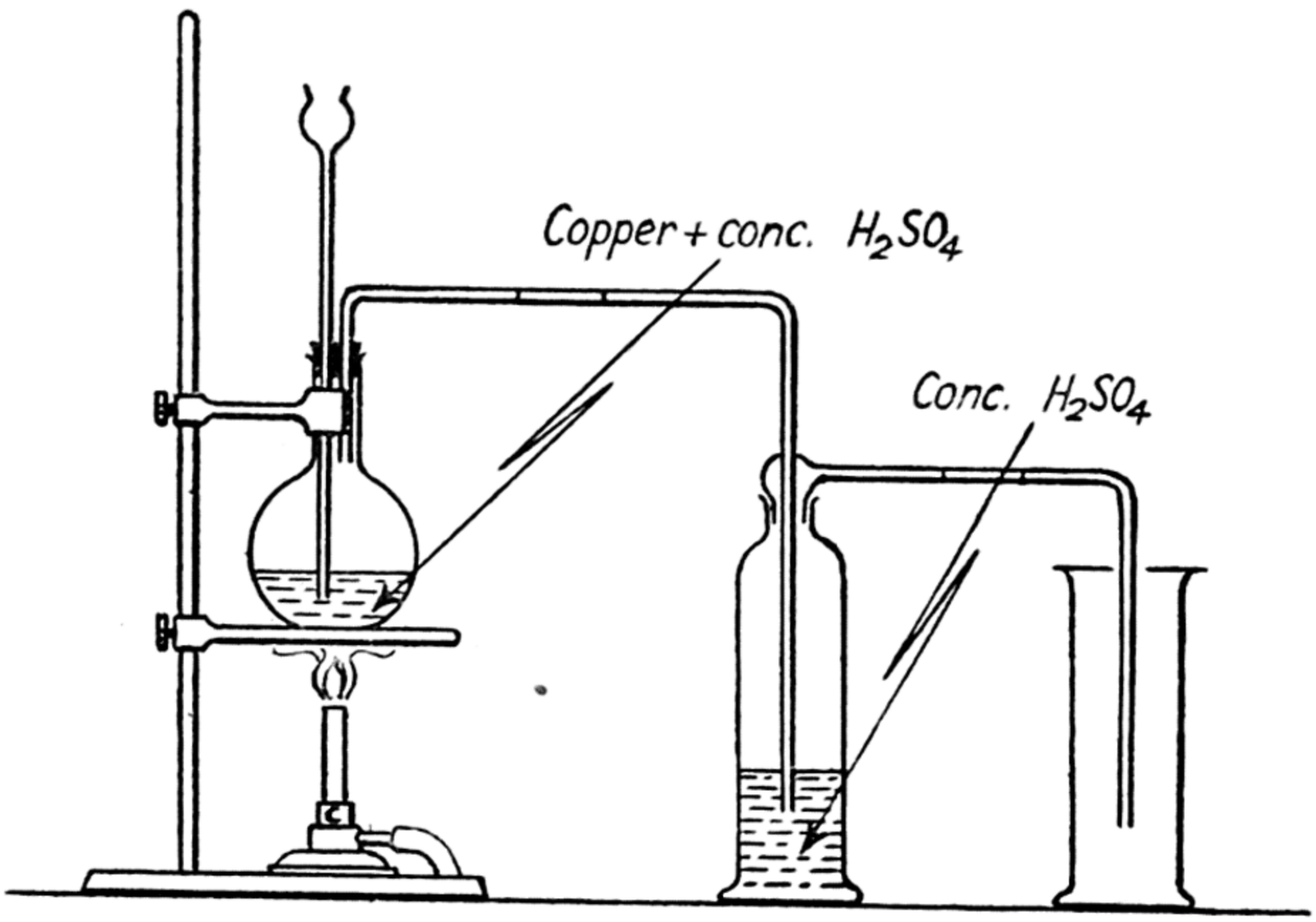


FIG. 230. Preparation of Sulphur Dioxide

The reaction is not however as simple as this equation suggests, since sulphuretted hydrogen is also formed as evidenced by the formation of a black precipitate of copper sulphide. The mechanism of this further reduction is not clear, but it may possibly be represented by the equation—

$$4SO_2 + H_2SO_4 = H_2S + 4SO_3$$

Sulphur dioxide may be prepared pure by burning sulphur in carbon dioxide-free air, absorbing the sulphur dioxide in a solution of sodium hydroxide to form sodium sulphite and bisulphite, and then treating these latter with dilute acid under air-free conditions. Or, pure sodium sulphite crystals may be treated directly with dilute acid.

$$NaOH + SO_2 = NaHSO_3$$
$$NaHSO_3 + HCl = NaCl + H_2O + SO_2 \uparrow$$
$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2 \uparrow$$

Commercially, sulphur dioxide is prepared by burning sulphur or pyrites in air.

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 \uparrow$$

The sulphur dioxide prepared by any of the above methods may be collected (*a*) by upward displacement of air, since it is about twice as heavy as air, (*b*) by dissolving in water, (*c*) by liquefaction under pressure.

Physical Properties of Sulphur Dioxide. Sulphur dioxide is a colourless gas, with the characteristic odour of burning sulphur. It is heavier than air (vapour density is 32 compared with 14·4 for air), and is appreciably soluble in water, 1 ml of water dissolving 80 ml of the gas at 0°C. The solubility decreases with increase in temperature and the gas may be completely expelled by boiling the solution. It is easily liquefied, boiling at − 10°C under one atmosphere pressure, but boils at 18°C under three atmospheres pressure. For this reason, it is usually supplied for laboratory use as liquid sulphur dioxide in heavy glass syphons, and like ammonia and carbon dioxide it finds extensive use in refrigeration plant.

Sulphur dioxide is poisonous, although some people appear more allergic to it than others. It causes inflammation of the lungs and induces asthmatical complaints.

Liquid sulphur dioxide, like water, is an ionizing solvent; that is, it dissolves certain compounds to give solutions which conduct electricity. Investigation of such solutions has both extended our knowledge of electrolytes and also led to a wider view of the concept of acids and bases.

Chemical Properties of Sulphur Dioxide. Like carbon dioxide, sulphur dioxide neither burns nor supports combustion. The exceptions are strongly burning sodium, potassium, magnesium, etc., where presumably the heat of the reaction is sufficient to dissociate the gas into sulphur and free oxygen.

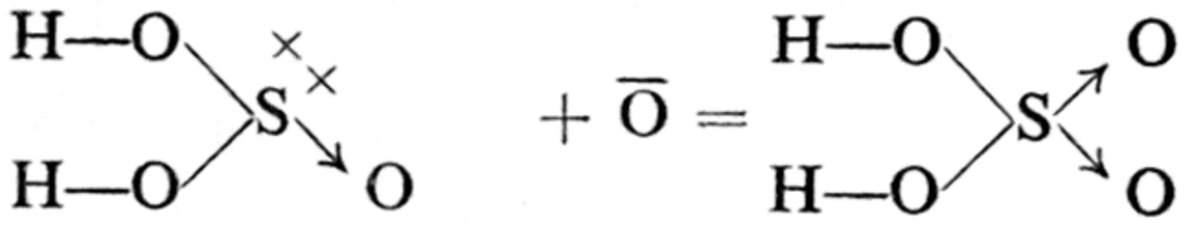
$$3Mg + SO_2 = 2MgO + MgS$$

The solution of sulphur dioxide in water is a weak dibasic acid, known as *sulphurous acid*, H_2SO_3. Both normal and acid sulphites are well known, but less common are the metabisulphites such as potassium metabisulphite, $K_2S_2O_5$. The reducing properties of sulphur dioxide in presence of water are attributed to the ease with which sulphurous acid may be converted to sulphuric acid—

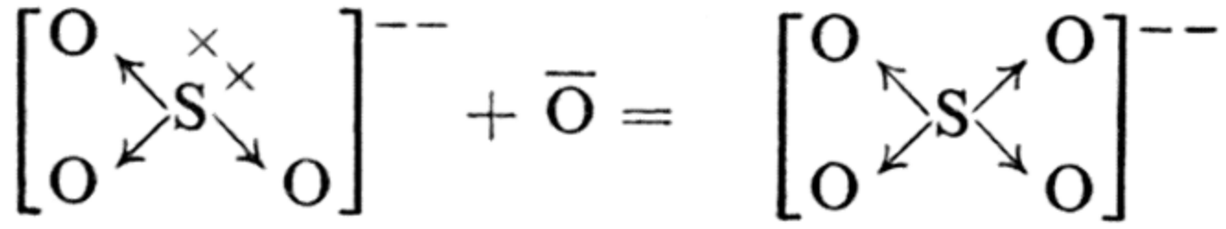
$$H_2SO_3 + \overline{O} = H_2SO_4$$

and this, in its turn is attributed to the presence of a "lone-pair" of electrons on the sulphur atom which enables it to add on another atom by forming a co-ordinate link. If the additional atom is oxygen, then sulphuric

acid or sulphates are formed; if sulphur, then thiosulphuric acid or thiosulphates are formed.



or



Similarly $$Na_2SO_3 + S \rightarrow \underset{\text{sodium thiosulphate}}{Na_2S_2O_3}$$

Thus solutions of sulphur dioxide are reducing agents; they reduce hydrogen peroxide, the halogens, ferric salts, chromates, dichromates and permanganates, etc. Permanganate solutions are decolorized, chromate and dichromate solutions assume the characteristic green colour of the chromic salt whilst ferric solutions become almost colourless (very pale green) due to the formation of ferrous salts. Note that in all these reactions, the sulphurous acid is oxidized to sulphuric acid, and that this behaviour is the basis of the commercial preparation of sulphuric acid from sulphur dioxide or sulphurous acid by the Lead Chamber Process, the oxidant in this case being nitrogen peroxide.

$$H_2SO_3 + NO_2 = H_2SO_4 + NO$$

The procedure for constructing the correct equations for these and other reactions has been described in connexion with sulphuretted hydrogen. The student should satisfy himself, by applying the same methods, that the following equations are correctly balanced—

$$2KMnO_4 + 2H_2O + 5SO_2 = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$
$$Cl_2 + 2H_2O + SO_2 = 2HCl + H_2SO_4$$
$$2K_2CrO_4 + 2H_2SO_4 + 3SO_2 = 2K_2SO_4 + Cr_2(SO_4)_3 + 2H_2O$$
$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
$$Fe_2(SO_4)_3 + 2H_2O + SO_2 = 2FeSO_4 + 2H_2SO_4$$

The bleaching action of sulphur dioxide in solution is another example of the ease with which sulphurous acid is oxidized—

$$\underbrace{H_2SO_3 + O}_{H_2SO_4} \quad \underbrace{H_2 + \text{Colour}}_{\text{Colourless leuco compound}}$$

Washing, air and sunlight slowly restore the colour, however.

The reaction of sulphur dioxide with sulphuretted hydrogen is unexpected—

$$2H_2S + SO_2 = 2H_2O + 3S\downarrow$$

This reaction, which occurs simply on mixing the gases, but not if they are thoroughly dry, suggests that the sulphur dioxide is behaving as an oxidizing agent. More probably, it indicates that the compound formed by hydrogen and oxygen is more stable than the compounds formed by these elements with sulphur.

Sulphur dioxide gas will combine directly with certain peroxides suitably heated, for example in a hard-glass tube, to initiate the reaction. The reaction is exothermic, and the heat liberated is sufficient to raise the mass to incandescence.

$$PbO_2 + SO_2 = \underset{\text{lead sulphate}}{PbSO_4}$$

Sulphur dioxide gas will also combine directly with chlorine, bromine and fluorine, particularly in the presence of camphor as catalyst, to form the corresponding sulphuryl halides—

$$SO_2 + Cl_2 = \underset{\text{sulphuryl chloride}}{SO_2Cl_2}$$

The direct oxidation of sulphur dioxide gas to sulphur trioxide does not occur at ordinary temperatures. It requires a relatively high temperature and is facilitated by the presence of a catalyst (*see* "The Contact Process," p. 755).

Formula of Sulphur Dioxide. Since sulphur burns in oxygen to form sulphur dioxide, it follows that only these two elements are present, so that the formula is S_xO_y. In this reaction, one volume of oxygen produces one volume of sulphur dioxide, so that, by Avogadro's Hypothesis—

$$\text{one molecule of } O_2 \rightarrow \text{one molecule of } S_xO_y$$

Hence $y = 2$, and formula is S_xO_2

Since, however, the vapour density of sulphur dioxide is 32, the molecular weight is 64. The formula is therefore SO_2.

Detection and Determination of Sulphur Dioxide. Sulphur dioxide may be recognized by (*a*) its smell, (*b*) the decoloration of permanganate and iodine solutions, (*c*) its action on chromate and dichromate solutions which it turns green, and (*d*) by its reaction with barium chloride solution with which it gives a white precipitate of barium sulphite. The latter may be distinguished from the similar white precipitate formed by sulphates by its ready solubility in dilute acids.

The concentrations of solutions of sulphur dioxide in water may be

determined by running in standard iodine solution from a burette into a measured volume of the sulphur dioxide solution until the iodine is no longer decolorized, as indicated by the appearance of the blue colour of added starch indicator.

$$SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI$$

Uses of Sulphur Dioxide. (*a*) Stoving rooms after infectious diseases, (*b*) bleaching wool, silk and straw, (*c*) manufacture of sulphuric acid, sulphites and bi-sulphites, etc., (*d*) as the inert atmosphere in the electrolytic method for obtaining magnesium and also in making magnesium-alloy castings (*see* p. 495).

Sulphurous Acid, H_2SO_3, is known only in weak aqueous solution, and is produced, for example, when sulphur dioxide is dissolved in water. It is a weak dibasic acid and is a reducing agent. The salts, known as sulphites, are also reducing agents, and on heating they undergo a self oxidation-reduction reaction to form sulphate and sulphide—

$$4Na_2SO_3 = 3Na_2SO_4 + Na_2S$$

Normal sulphites are alkaline in solution, but the acid (or hydrogen) sulphites are feebly acidic due to the dissociation of the HSO_3^- ion. Both sodium sulphite and sodium bisulphite are produced commercially by the action of sulphur dioxide on crystals of sodium carbonate or its solution in water—

$$Na_2CO_3 + SO_2 = Na_2SO_3 + CO_2\uparrow$$
$$Na_2SO_3 + H_2O + SO_2 = 2NaHSO_3$$

The acid solution of sodium bisulphite which is ultimately obtained is sold as such, but some is converted into the normal sulphite by neutralizing the solution by adding sodium carbonate at the boiling-point—

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + H_2O + CO_2$$

The resulting solution is then concentrated and allowed to crystallize to form $Na_2SO_3 \cdot 7H_2O$ if the temperature is below 22°C, or Na_2SO_3 if above this temperature. Sodium sulphite is used as a mild bleaching agent for silk and woollen goods, as an antichlor after bleaching cloth, paper pulp, etc., with chlorine, and in photographic developers to resist atmospheric oxidation of the amidol, metol, etc. Sodium bisulphite is used extensively in the manufacture of paper from wood pulp; hot solutions possess the valuable property of dissolving resins and gums contained in the wood, without affecting the important cellulose fibres. Most paper, nowadays, is manufactured from the resulting "sulphite" pulp.

Sulphur Trioxide (Sulphuric Anhydride), SO_3. Sulphur trioxide is liberated by the action of heat on such compounds as pyro-sulphuric

acid, $H_2S_2O_7$ and its salts, sodium bi-sulphate, ferrous (and ferric) sulphate—

$$H_2S_2O_7 = H_2SO_4 + SO_3\uparrow$$
$$2NaHSO_4 = Na_2S_2O_7 + H_2O$$
$$Na_2S_2O_7 = Na_2SO_4 + SO_3\uparrow$$
$$2FeSO_4 = Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

It may be prepared by dehydrating concentrated sulphuric acid by the action of phosphorus pentoxide. If the reaction is carried out by heating a mixture of phosphorus pentoxide and concentrated sulphuric acid in a retort the sulphur trioxide evolved may be condensed and collected.

$$H_2SO_4 - H_2O = SO_3$$

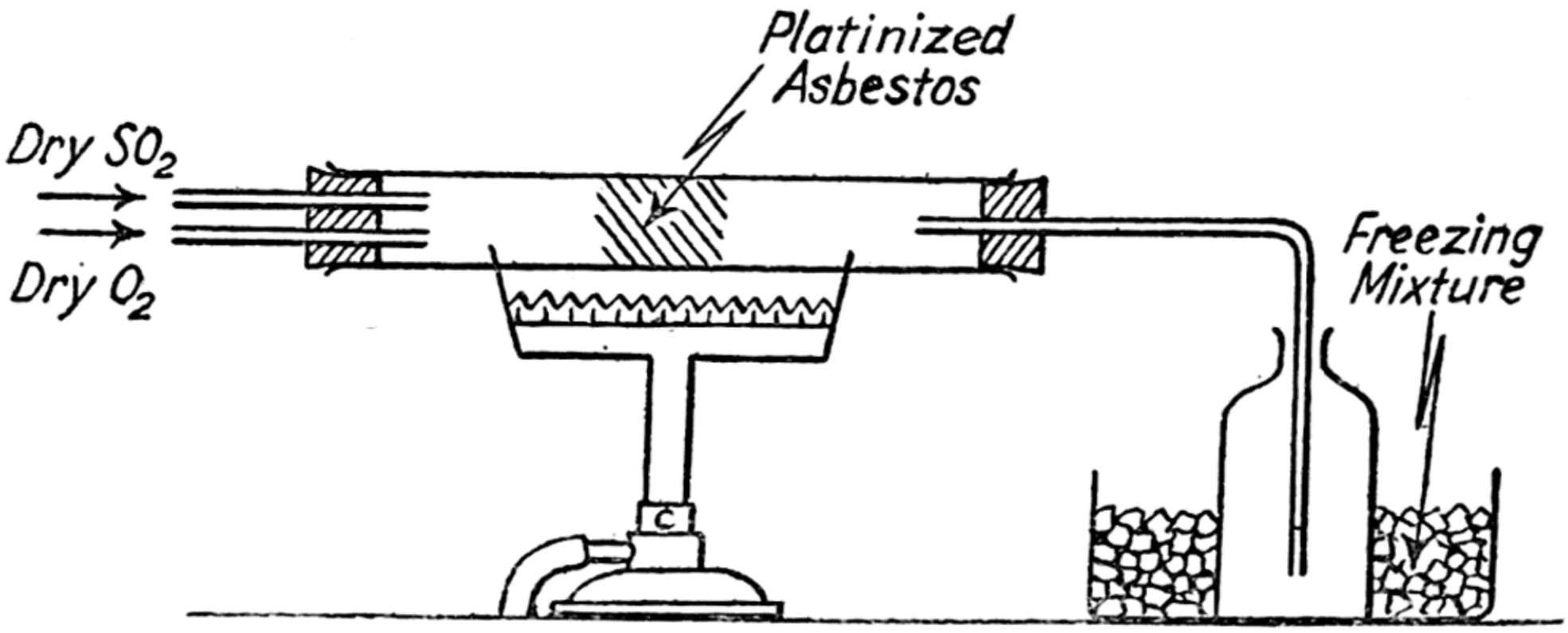


FIG. 231. Preparation of Sulphur Trioxide

The *Contact Process* produces sulphur trioxide on a large scale (in the manufacture of sulphuric acid) by the direct combination of sulphur dioxide and oxygen at 450°–600°C in presence of a suitable catalyst (*see* p. 219). The reaction may be carried out in the laboratory by passing sulphur dioxide and oxygen gases through concentrated sulphuric acid to dry them, and then through a hard glass tube containing a plug of platinized asbestos which is heated. The issuing gases are then passed through a tube immersed in a freezing mixture to condense the sulphur trioxide—

$$2SO_2 + O_2 = 2SO_3$$

Properties of Sulphur Trioxide. Two forms of sulphur trioxide are definitely known and a third has been reported. α-SO_3 is a colourless liquid boiling at 45°C and forming colourless needles at 16°–17°C. In presence of moist air it slowly changes to β-SO_3 an asbestos-like solid, which sublimes at 50°C.

The gas forms a dense fog in moist air consisting of fine droplets of

sulphuric acid, and the solid reacts vigorously with water (with a hissing sound) to form sulphuric and fuming sulphuric acids. Although the solution of sulphur trioxide in water is a very strong acid, the perfectly dry gas clearly is not an acid (it contains no hydrogen).

If sulphur trioxide is passed over heated oxides of calcium, magnesium, or barium, a vigorous reaction occurs and the mass becomes incandescent—

$$MgO + SO_3 = MgSO_4$$

The gas is not stable on heating, but tends to dissociate into sulphur dioxide and oxygen. The reaction—

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

is in fact reversible, but a discussion of this reaction will be deferred to the section on the Contact Process.

Stabilized and partly stabilized forms of sulphur trioxide are now manufactured and sold commercially. These consist of the gamma and beta modifications, with compounds such as thionyl chloride ($SOCl_2$) as the stabilizers.

Other Oxides of Sulphur. The following additional oxides of sulphur have been reported—

Sulphur monoxide, SO	Sulphur sesquioxide, S_2O_3
Sulphur tetroxide, SO_4	Sulphur heptoxide, S_2O_7

They are prepared only with difficulty and are all unstable at room temperatures.

Sulphuric Acid, H_2SO_4. Historically, the acid was first produced commercially by Ward at Richmond in 1736. A mixture of sulphur and potassium nitrate was allowed to burn on an iron dish in the mouth of a large glass vessel containing a little water. A wooden bung was inserted during the combustion, and periodically removed to admit fresh air. The solution of the resulting gases produced sulphuric acid, which was later further concentrated by distillation. Such was the beginning of a major industry which now produces millions of gallons of sulphuric acid each year. There are two different processes in operation nowadays; the Lead Chamber Process, which is essentially a development of Ward's process, and the Contact Process which produces sulphur trioxide as an intermediate in the manufacture of the acid.

Lead Chamber Process. This process is based on the oxidation of sulphur dioxide in presence of water to sulphuric acid. The oxidant is nitrogen peroxide—

$$H_2SO_3 + NO_2 = H_2SO_4 + NO$$

The resulting nitric oxide combines with oxygen to reform nitrogen

peroxide, so that theoretically a small quantity of nitrogen peroxide initially present should produce a large quantity of sulphuric acid.

$$2NO + O_2 = 2NO_2$$

The actual reactions are somewhat more complex than these equations suggest, and intermediate compounds such as $H_2SO_4 . NO$ or $H_2SO_3 . NO_2$, known variously as *nitrosyl sulphuric acid*, *chamber crystals*, etc., are known to be formed during the process.

Reference to the accompanying diagram shows that the process is made up of the following units or stages—

(*a*) Production of sulphur dioxide; (*b*) production of oxides of nitrogen; (*c*) the Glover Tower; (*d*) the Lead Chambers; and (*e*) the Gay Lussac Tower.

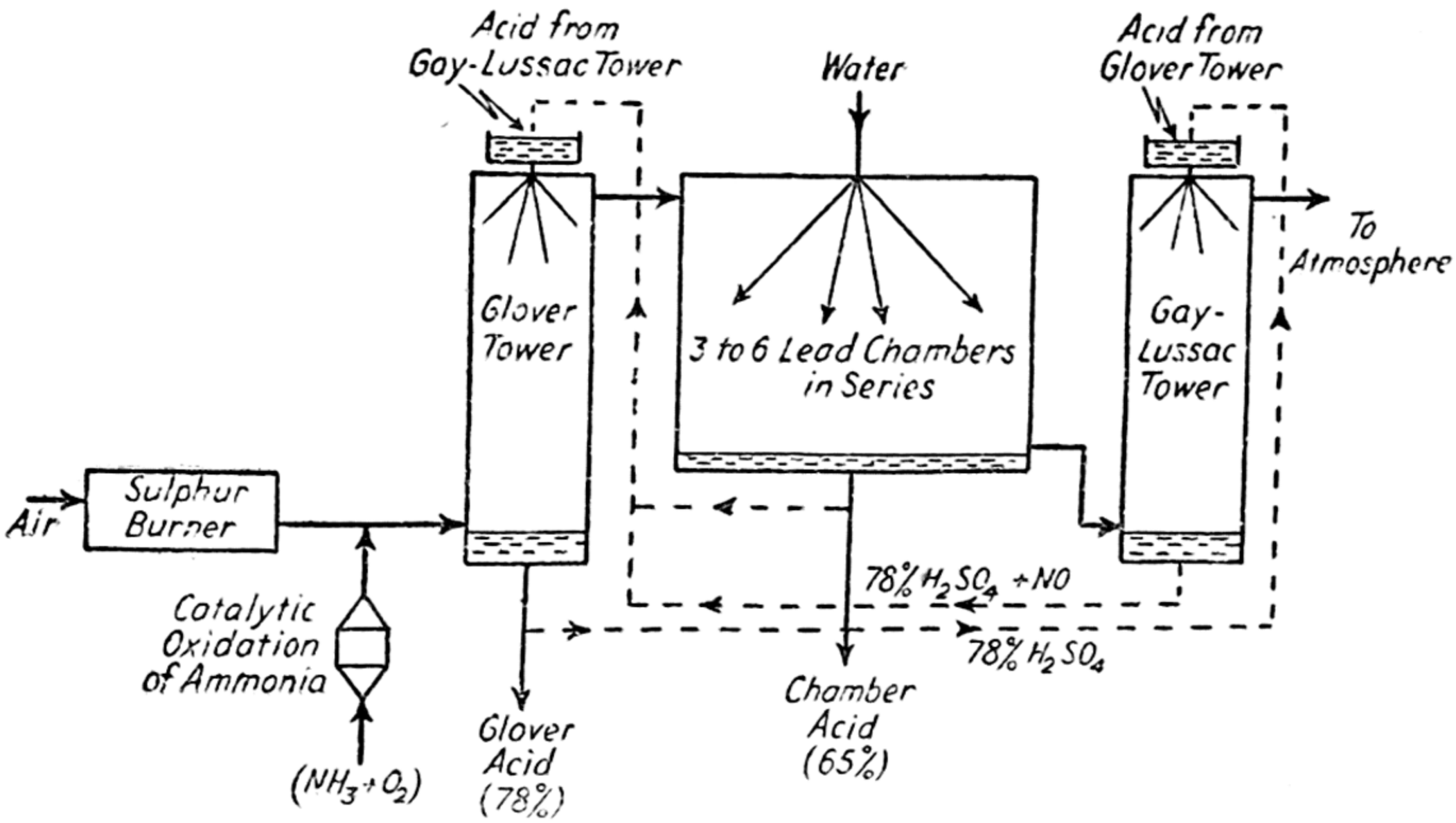


FIG. 232. Lead Chamber Process

(*a*) *Production of Sulphur Dioxide.* This is produced either by burning sulphur in air in specially designed burners to increase the efficiency of the oxidation, or by roasting pyrites or other sulphide ores such as zinc blende in air; the sulphur dioxide in the latter case might be a by-product of the metallurgical operation.

(*b*) *Production of Oxides of Nitrogen.* These are produced either by the action of sulphuric acid on sodium nitrate in the nitre pots, or by the catalytic oxidation of ammonia. The modern practice is to use the latter method. The ammonia is mixed with air and passed through a platinum gauze catalyst which is maintained at about 1000°C by the heat of the reaction—

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$
$$2NO + O_2 = 2NO_2$$

(*c*) *The Glover Tower.* These brick- or lead-lined steel towers are packed with ceramic material, such as hard burnt brick or tile. Down this tower flows 78 per cent sulphuric acid containing oxides of nitrogen recovered in the Gay Lussac Tower and also some 62 per cent Chamber sulphuric acid. The hot gases (sulphur dioxide, oxides of nitrogen, air) enter the tower near the base, are cooled as they pass up and eventually pass into the lead chambers at a temperature of about 100°C. In this tower, about 10 per cent conversion of the sulphur dioxide to sulphuric acid occurs, the oxides of nitrogen are recovered from the Gay Lussac acid, some concentration of the descending sulphuric acid occurs, and the 78 per cent acid which collects at the bottom is suitable for the recovery of the oxides of nitrogen in the Gay Lussac towers.

(*d*) *The Lead Chambers.* These consist of several large, sheet lead chambers. A very fine spray of water is injected from the roof to form the bulk of the sulphuric acid the concentration of which is about 65 per cent. The concentration is not allowed to exceed this value since more concentrated acid tends to dissolve the lead of the chambers and also removes a considerable proportion of the oxides of nitrogen on which the economic success of the process depends. In modern plant special precautions are taken to dissipate the heat of the reaction. Thus, in the Mills-Packard plant, the chambers are in the shape of truncated cones with provision for water cooling on the outsides. In the Gaillard-Parrish plant, the "chambers" consist of a steel-frame lead-lined cylindrical chamber cooled on the *inside* by spraying the walls with finely divided pre-cooled chamber acid.

(*e*) *The Gay Lussac Tower.* These towers, which are taller and narrower than the Glover towers serve the very important purpose of recovering the oxides of nitrogen from the spent gases. The waste gases, now at a temperature of about 60°C, meet, as they pass up the tower, a descending stream of cold 78 per cent acid from the Glover Tower. The latter acid dissolves the oxides of nitrogen to form "Gay-Lussac Acid" which is then pumped to the top of the Glover Tower. The amount of acid used in this cyclic operation between the Glover and Gay Lussac Towers to recover the relatively expensive oxides of nitrogen amounts to about three or four times the daily production of sulphuric acid by the plant.

Concentration and Purification. The lead chambers produce the bulk of the acid (concentration about 65 per cent), but a smaller quantity of 78 per cent cent acid is recovered from the Glover towers. The acid may be purified if necessary by diluting and treating with sulphuretted hydrogen to precipitate arsenic as its sulphide, followed by distillation with a little added ammonium sulphate, when the lead sulphate is left behind and any dissolved oxides of nitrogen are reduced to nitrogen—

$$(NH_4)_2SO_4 + N_2O_3 = 2N_2 + H_2SO_4 + 3H_2O$$

Most of the acid is used as produced, for example in the manufacture of

superphosphate, ammonium sulphate, etc., but for other purposes a more concentrated acid may be required.

The 78 per cent acid may be concentrated to about 93 per cent acid by heating, but stronger acids are more usually produced by adding oleum or sulphur trioxide from a Contact Plant.

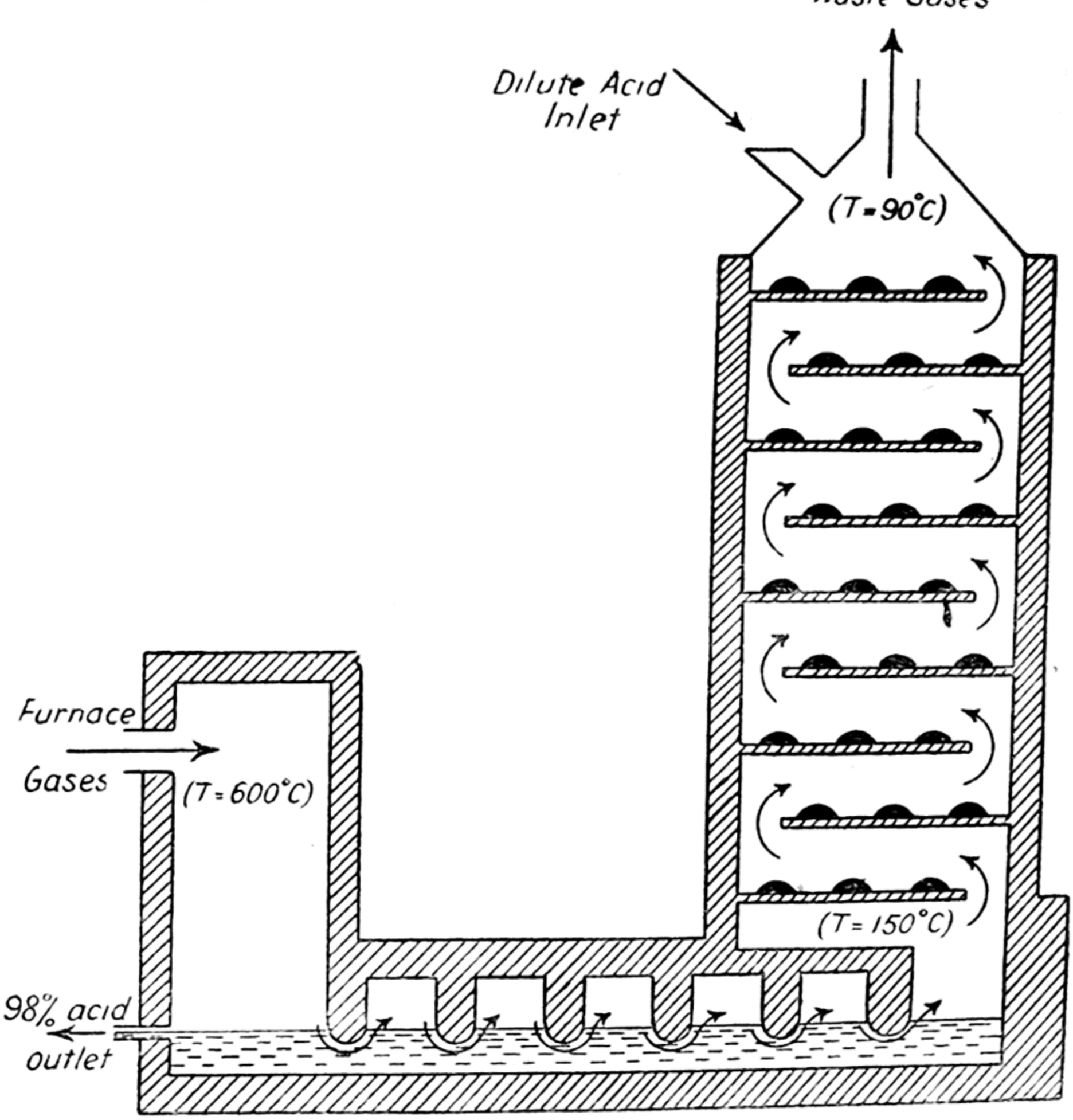


FIG. 233. Kessler Concentrator

The older method of concentrating the acid consisted in allowing the acid to pass in a cascade system down a stair-way of silica crucibles against an ascending stream of hot furnace gases. The modern methods either concentrate the acid by the action of hot furnace gases on a descending spray of the acid in a large tower as in the Gaillard Concentrator or in the Kessler Concentrator as shown in the accompanying diagram, or the acid is heated under vacuum by superheated steam. When concentrated acids are required however, it appears to be increasingly the modern practice

to prepare the acid directly by the Contact process. The above concentrators then become important in the recovery and reconcentration of process acids.

The Contact Process. Whereas the Lead Chamber Process involves the relatively easy oxidation of a solution of sulphur dioxide in water directly to sulphuric acid, the Contact Process attempts the much more difficult direct oxidation of dry sulphur dioxide gas to sulphur trioxide—

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45\,900 \text{ cal.}$$

Fig. 234 shows the effect of temperature on the equilibrium yield of sulphur trioxide. As might be expected from Le Chatelier's Principle,

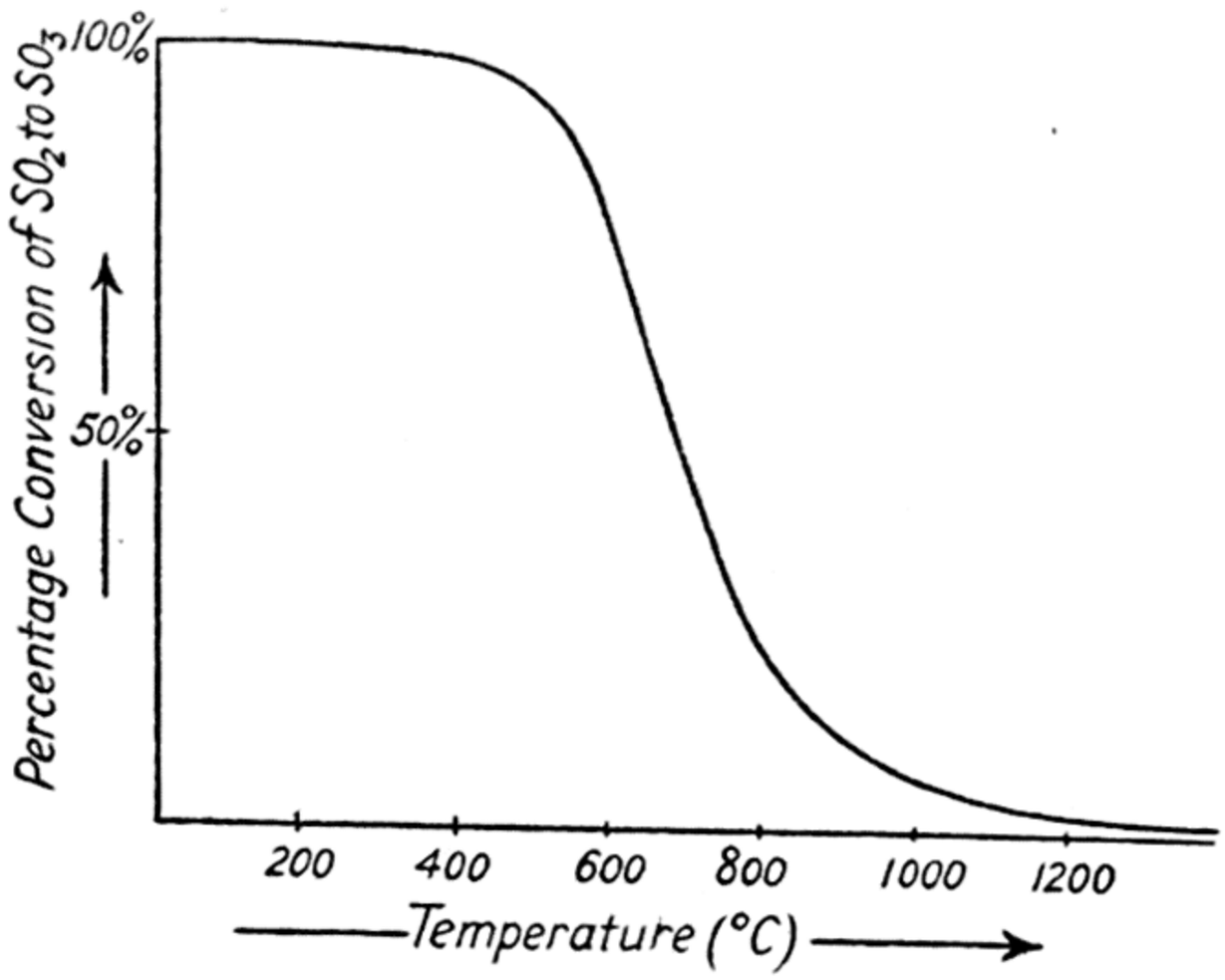


FIG. 234. Variation of the Percentage Conversion of Sulphur Dioxide to Sulphur Trioxide with Temperature

since the reaction is exothermic the equilibrium yield will be increased by decrease in temperature. Although almost a 100 per cent yield is obtained at 400°C, the time required to reach this equilibrium state is very long, too long for the process to be economical. There are two ways of speeding up the rate of a reaction, namely, by increasing the temperature and by the use of a catalyst. In the present case, increase of temperature will also reduce the equilibrium yield of sulphur trioxide, and for this reason only a relatively small such increase will be economical. The alternative method is to use a suitable catalyst. A *catalyst* is a substance which speeds up the rate of a reaction *without itself being chemically changed*; but, since it speeds up both the forward and back reactions by the same amount, the position of equilibrium is not altered. The catalyst thus considerably reduces the time required to reach equilibrium but does not alter the position of equilibrium from the value it would have in the absence of the catalyst. The reaction is therefore carried out at a

temperature of 450°–600°C in presence of a catalyst. By applying the Law of Mass Action to the equilibrium, we find that

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

whence, $$[SO_3]^2 = K \times [SO_2]^2 \times [O_2]$$

It follows, therefore, that an increase in the concentration of either the sulphur dioxide or of the oxygen will increase the equilibrium yield of sulphur trioxide. In practice, since oxygen is much cheaper than sulphur dioxide, a somewhat higher concentration of oxygen is used, the sulphur dioxide concentration being limited to 7–10 per cent depending upon the catalyst.

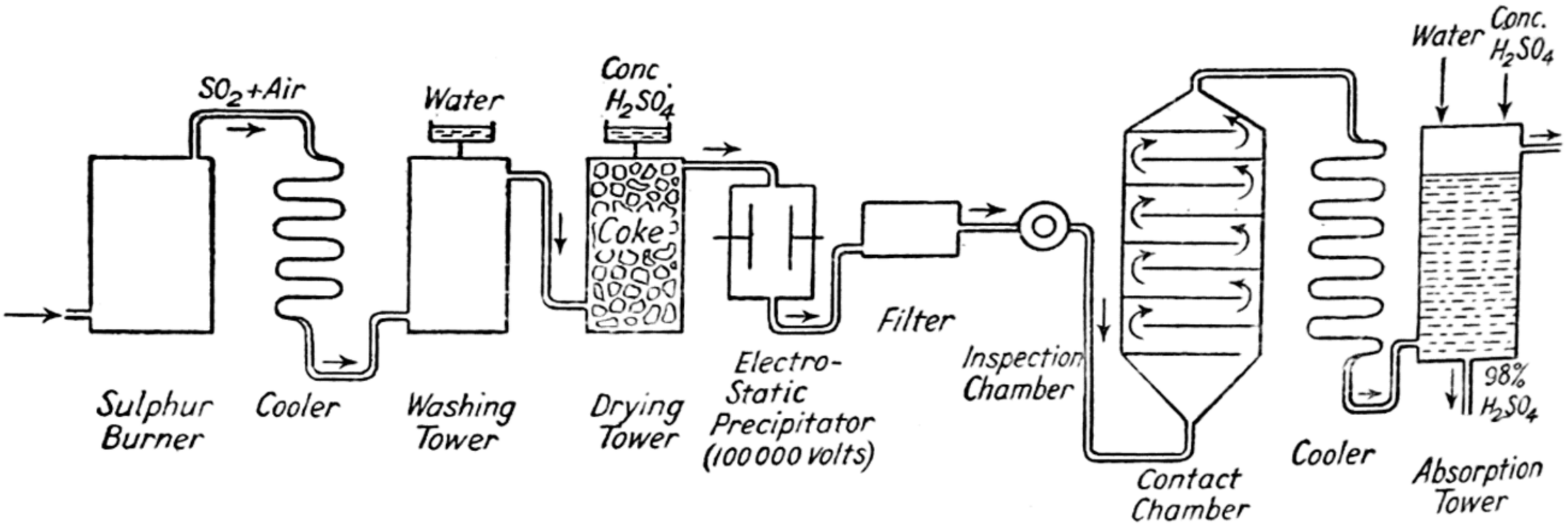


FIG. 235. Contact Process

Further consideration of the above value of K shows that, by Le Chatelier's Principle, the equilibrium yield of sulphur trioxide may be increased by carrying out the reaction under pressure. The effect is, however, so small that the expense of the additional plant does not justify any increase in pressure; the process is therefore carried out at ordinary pressures.

The accompanying diagram shows that the process is composed of the following "units" or stages; (*a*) preparation of sulphur dioxide; (*b*) purification of sulphur dioxide; (*c*) reaction vessel or "converters"; (*d*) conversion of the sulphur trioxide into sulphuric acid.

(*a*) *Preparation of Sulphur Dioxide.* *See* Lead Chamber Process.

(*b*) *Purification of the Sulphur Dioxide.* The sulphur dioxide has to be thoroughly purified and dried before it is allowed to come into contact with the catalyst. It may contain dust, arsenic, selenium, chlorine and bromine (if pyrites be used). A typical treatment of the sulphur dioxide includes removal of dust by passing the gas through a centrifugal separator followed by a Lodge-Cottrell electrostatic dust precipitator (*see* diagram), then up a tower filled with acid-resisting packing which is sprayed from the top with 40 per cent sulphuric acid (to remove arsenic and part of the

chlorine), through a second Lodge-Cottrell plant to remove acid mist, through coke-filters and finally over concentrated sulphuric acid to dry it.

(*c*) *Contact Chambers*. The conversion of the sulphur dioxide to sulphur trioxide is nowadays mostly carried out in two stages; the first chamber or converter works at a higher temperature (500°–600°C) to ensure a rapid conversion to about 75 per cent sulphur trioxide, whilst the second converter works at a lower temperature (400°–450°C). The time required to reach equilibrium in the second converter is much longer but results in a more or less complete conversion of the sulphur dioxide to sulphur trioxide.

The catalyst is either finely divided platinum or vanadium (in the form of ammonium vanadate or vanadium pentoxide). The platinum is supported on suitable carriers which must be porous, inert to the gases at high temperatures, refractory, and strong. Examples include asbestos, silica-gel, and calcined magnesium sulphate. In the Mannheim two-stage process, the catalyst in the first converter is burnt pyrites, that is ferric oxide containing a little cupric oxide, and the operating temperature is about 700°C. At this higher temperature, the conversion is about 65 per cent. Any arsenious oxide present is removed at this stage as ferric arsenate, and the issuing gases, after removal of the sulphur trioxide, are passed through a platinum catalyst converter to complete the oxidation.

The relative merits of platinum and vanadium as catalysts are briefly—

(i) Some 90 per cent of the platinum may be recovered whereas the vanadium has no salvage value.

(ii) Platinum operates successfully with a higher concentration of sulphur dioxide than is possible with vanadium (8–10 per cent, cf. 7–8 per cent).

(iii) Platinum catalysts are easily poisoned, particularly by arsenic; vanadium catalysts are not.

(iv) Vanadium catalysts have a longer active life than platinum catalysts, and are also less fragile, permitting easier handling in use.

(v) The initial cost of vanadium is less than that of platinum, and the cost is likely to be even less in the future.

(*d*) *Conversion of the Sulphur Trioxide into Sulphuric Acid.* Water cannot be used to absorb the sulphur trioxide because an acid mist forms which in practice is found to be almost impossible to absorb or condense. It was soon found that the best absorbent was 98·5–99 per cent sulphuric acid. In practice, the sulphur trioxide is allowed *either* to bubble into acid of this concentration with controlled addition of either dilute acid or water to maintain the concentration at this value, *or*, more usually, the same result is obtained by absorbing the sulphur trioxide by passing it up a tower down which flows concentrated sulphuric acid. Direct solution of sulphur trioxide in concentrated sulphuric acid produces the oleums, for example, 20 per cent oleum which is a solution of 20 per cent of SO_3 by weight in 100 per cent sulphuric acid.

Comparison of the Chamber and Contact Processes. Chemically, the Chamber Process involves the relatively easy oxidation of sulphurous acid by nitrogen peroxide at about 100°C—

$$H_2SO_3 + NO_2 = H_2SO_4 + NO$$

The Contact Process involves the more difficult direct oxidation of sulphur dioxide *gas* in presence of a catalyst at 450°–600°C, to form sulphur trioxide, which is subsequently converted into sulphuric acid.

$$2SO_2 + O_2 = 2SO_3$$

The Lead Chamber Process produces 65 per cent acid and smaller quantities of 78 per cent acid, which are used mainly in the manufacture of super-phosphate and to a smaller extent of ammonium sulphate (in gas-works). Concentration to produce a concentrated acid is much more difficult than is the converse process of diluting Contact acid. The Contact process produces a pure and concentrated sulphuric acid; that from the Lead Chamber process is neither pure nor concentrated.

The development of the Contact Process resulted from demands of the new dye-stuffs industry for fuming sulphuric acid for the manufacture of alizarin and other organic dyes. The modern trend is in the direction of more Contact sulphuric acid, and less Chamber acid, although the latter is not an obsolescent process—new plant are in fact being constructed.

Properties of Sulphuric Acid. Sulphuric acid is a strong dibasic acid. The 100 per cent acid melts at 10·5°C; on raising it to the boiling point some sulphur trioxide is evolved until at 317°C an acid of 98 per cent concentration distils unchanged. Solutions of sulphur trioxide in concentrated sulphuric acid produce the oleums. The following table shows the percentage and specific gravities of the various commercial sulphuric acids—

TABLE 105

Commercial Grades of Sulphuric Acid

Name	Sulphuric Acid	Specific Gravity	°Tw
Battery acid	33·4 per cent	1·250	50
Chamber acid	62–65 per cent	1·526	105
Glover acid	77·7 per cent	1·706	141
Oil of vitriol (B.O.V.)	93·2 per cent	1·835	167
98 per cent acid	98·0 per cent	1·841	168
Sulphuric acid or Monohydrate	100·0 per cent	1·835	167
20 per cent Oleum	20 per cent free SO_3	1·927	185
40 per cent Oleum (*see* p. 757)	40 per cent free SO_3	1·965	193
65 per cent Oleum	65 per cent free SO_3	1·990	198

Chemical Properties of Sulphuric Acid. Sulphuric acid is a powerful dehydrating agent, particularly towards organic compounds—

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} - 11H_2O = \underset{\substack{\text{sugar-}\\\text{carbon}}}{12C}$$

$$\underset{\text{formic acid}}{H\,.\,COOH} - H_2O = \underset{\substack{\text{carbon}\\\text{monoxide}}}{CO}$$

$$\underset{\text{oxalic acid}}{H_2C_2O_4} - H_2O = CO + CO_2$$

In these reactions, we speak of the concentrated sulphuric acid removing the elements of water, since the compounds do not contain water molecules as such in their molecular structure. Concentrated sulphuric acid is also used as a drying agent, but it may not be used for this purpose with gases which are basic (ammonia), or reducing agents (H_2S, SO_2, etc.).

When sulphuric acid is both hot and concentrated it is an oxidizing agent. It will dissolve most of the metals (not the noble metals), sulphur, carbon, and will liberate bromine and iodine from their salts or acids—

$$C + 2H_2SO_4 = CO_2\uparrow + 2SO_2\uparrow + 2H_2O$$

$$S + 2H_2SO_4 = 3SO_2\uparrow + 2H_2O$$

$$Cu + 2H_2SO_4 = SO_2\uparrow + CuSO_4 + 2H_2O$$

$$2HBr + H_2SO_4 = SO_2\uparrow + Br_2\uparrow + 2H_2O$$

Its relatively high boiling point accounts for its use in the preparation of nitric and hydrochloric acids from their salts on heating.

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3\uparrow$$

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl\uparrow$$

Since the nitric and hydrochloric acids escape on heating, the reactions should not be regarded as indicating that sulphuric acid is stronger than these two acids. Note, also, that the dehydrating action of the concentrated sulphuric acid results in these acids being liberated anhydrous.

Both sulphuric acid and some of its salts are decomposed when strongly heated. Thus, if sulphuric acid is allowed to fall on to a red-hot plate or is passed through a red-hot silica tube, then—

$$2H_2SO_4 = 2H_2O\uparrow + 2SO_2\uparrow + O_2\uparrow$$

The decomposition of ferrous sulphate has already been mentioned in connexion with sulphur trioxide—

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$$

Acid sulphates, such as sodium hydrogen sulphate, $NaHSO_4$, decompose

on heating to form first the pyrosulphate which then decomposes to form the normal sulphate and liberate sulphur trioxide—

$$2NaHSO_4 = Na_2S_2O_7 + H_2O$$

sodium pyrosulphate

$$Na_2S_2O_7 = Na_2SO_4 + SO_3 \uparrow$$

Sulphates may be reduced to the sulphides by heating strongly with carbon—

$$Na_2SO_4 + 4C = Na_2S + 4CO \uparrow$$

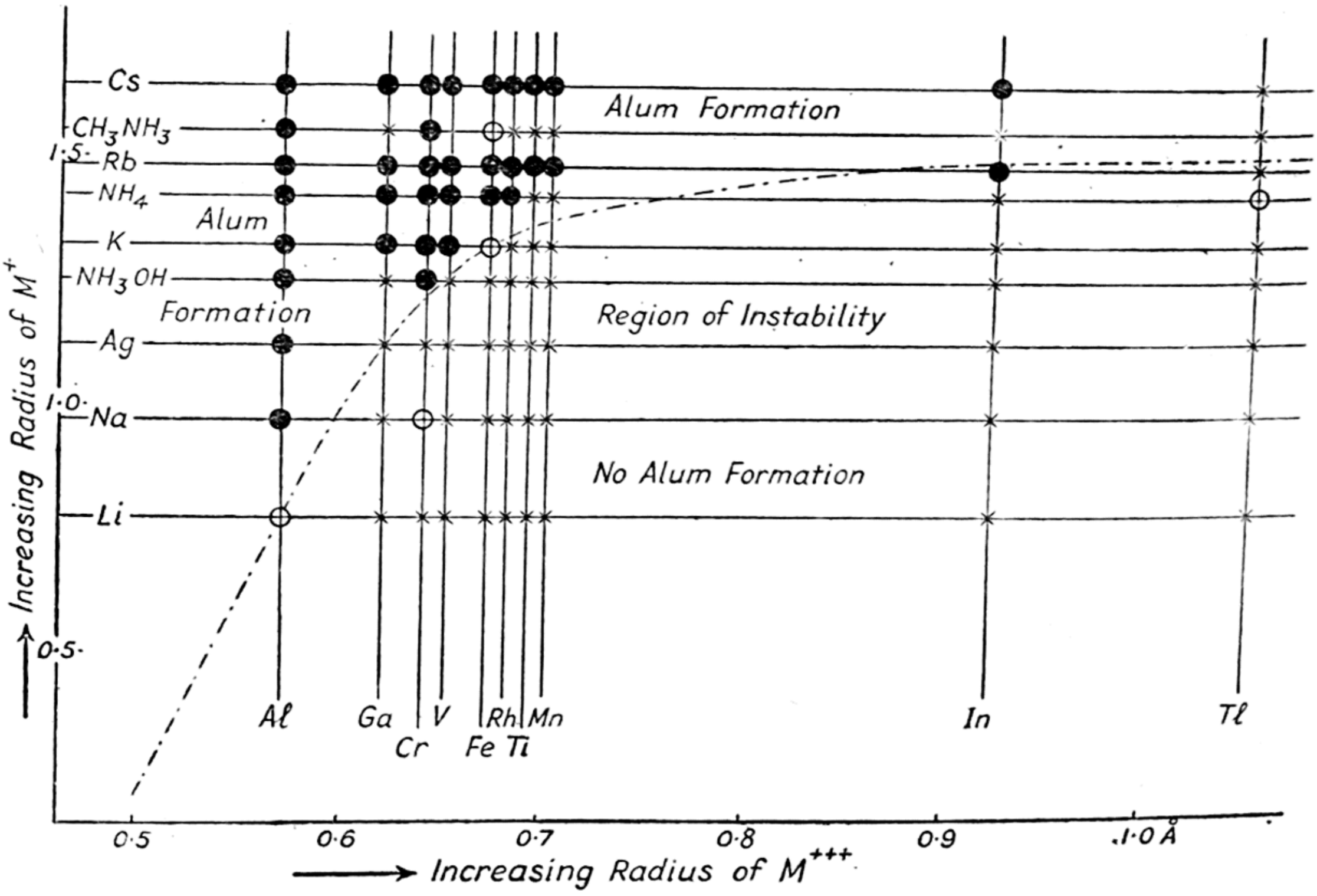


FIG. 236. The Alums as a Function of Radii of M^+ and M^{+++}

● Known ○ Reported × Not reported

As a class the sulphates are soluble, the principle exceptions being the sulphates of strontium, barium, lead and mercurous mercury. Most of the soluble sulphates crystallize from water as hydrates; examples include—

$CuSO_4 . 5H_2O$, blue vitriol; $FeSO_4 . 7H_2O$, green vitriol;

$MgSO_4 . 7H_2O$, Epsom Salts; $Na_2SO_4 . 10H_2O$ Glauber's Salt.

A large number of double sulphates are also known, as indicated by the general formulae—

$M^+{}_2SO_4 . M^{++}SO_4 . 6H_2O$; for example, $(NH_4)_2SO_4 . FeSO_4 . 6H_2O$

$M^+{}_2SO_4 . M_2{}^{+++}(SO_4)_3 . 24H_2O$, known as the *Alums*.

The extent of the alum structure is well indicated by the graphical illustration (p. 760) showing the dependency of the structure on the sizes of the univalent and trivalent cations. The reader is referred to page 413 for a fuller discussion of hydrates, and the mode of linkage of the molecules of water of hydration.

TABLE 106

Production and Uses of Sulphuric Acid

(*a*) *Production*—

Chamber process	153,243 tons (calculated as 100 per cent H_2SO_4)
Contact process	237,859 tons (calculated as 100 per cent H_2SO_4)

(*b*) *Raw Materials*—

	tons
Pyrites	49,473
Spent oxide (ex Gas works)	54,705
Sulphur and H_2S	66,658
Zinc concentrates	47,592

(*c*) *Consumption* (calculated as 100 per cent H_2SO_4)—

	tons
Superphosphates	90,634
Sulphate of ammonia	67,522
Rayon and transparent paper	52,054
Paint and lithopone	27,536
Iron pickling (including tin plate)	22,543
Dyestuffs and intermediates	18,985
Hydrochloric acid	14,692
Oil refining and petroleum products	14,645
Explosives	5,280
Textile uses	5,004
Sulphates of copper, nickel, etc.	4,844
Tar and benzole	3,912
Bichromate and chromic acid	3,384
Soap and glycerine	3,183
Plastics, not otherwise classified	3,132
Bromine	3,018
Drugs and fine chemicals	2,872
Hydrofluoric acid	2,574
Oils (vegetable)	2,374
Sulphate of magnesium	1,176
Phosphates (industrial)	708
Copper pickling	565
Metal extraction	481
Agricultural purposes	207
Glue, gelatine and size	117
Unclassified	38,134

Uses of Sulphuric Acid. Sulphuric acid finds its most extensive applications nowadays in the manufacture of superphosphate fertilizers; in

petroleum processing and refining; as a sulphonating agent and admixed with nitric acid as a nitrating acid in organic chemistry in the manufacture of dyes, explosives, etc. (T.N.T., tetryl, cyclonite, etc.); in the metallurgical industries for cleaning brass, bronze, copper, etc., and for "pickling" iron and steel; and also in the recovery of many metals from their ores. The uses of the acid are in fact so wide that it is extremely probable that they have never all been collected in one table.

Formerly considerable quantities of the acid were used in the manufacture of nitric acid (now largely replaced by the direct oxidation of synthetic ammonia), in the Le Blanc Process (now replaced by the Ammonia-Soda Process), in the manufacture of phosphatic materials from phosphate rock (now largely replaced by the electro-thermal acid-exchange using sand), and finally in the production of ammonium sulphate, which is now produced extensively by double decomposition between ammonium carbonate and calcium sulphate. To offset these changes, newer outlets for the acid include its increasing use in the artificial silk industry, as a catalyst in many organic reactions, and in the ever-growing petroleum industries.

The figures shown on p. 761 taken from the quarterly statement issued by the National Sulphuric Acid Association for the period, 1st January to 31st March, 1951, give some idea of the quantities of sulphuric acid produced in the Chamber and Contact processes and also of the various uses to which this acid is put.

Other Acids of Sulphur and their Salts

Hyposulphurous Acid, $H_2S_2O_4$, is known only in weak aqueous solution and is one of the most powerful reducing agents known. Sodium hydrosulphite (note, *not* hyposulphite) is, however, stable under perfectly dry conditions. It is manufactured commercially by passing sulphur dioxide gas into a suspension of good quality zinc powder which is kept continuously stirred. The zinc passes into solution as zinc hydrosulphite, the temperature being about 30°C—

$$Zn + 2SO_2 = ZnS_2O_4$$

A solution of sodium carbonate is then added to precipitate zinc carbonate, and the resulting solution after filtration is treated with sodium chloride to salt out $Na_2S_2O_4 \cdot 2H_2O$—

$$ZnS_2O_4 + Na_2CO_3 = ZnCO_3 + Na_2S_2O_4$$

On raising the temperature to about 53°C the di-hydrate changes to the anhydrous form. This is collected, washed with alcohol, dried in vacuum ovens, and then packed in hermetically sealed containers.

Sodium hydrosulphite combines with formaldehyde (also a powerful reducing agent) to form $Na_2S_2O_4 \cdot 2CH_2O$. *Rongalite* and *Decrolin* are

the sodium and zinc salts respectively of the closely related formaldehyde sulphoxylates, and are used as reducing agents in dyeing, printing and bleaching.

Thiosulphuric Acid, $H_2S_2O_3$, is not known in the free state. Solutions in water slowly decompose, more rapidly on warming, to liberate free sulphur.

$$Na_2S_2O_3 + 2HCl = 2NaCl + (H_2S_2O_3)$$

$$(H_2S_2O_3) = H_2O + SO_2\uparrow + S\downarrow$$

Sodium thiosulphate, commonly but incorrectly known as "hypo," may be prepared by boiling a solution of sodium sulphite with sulphur—

$$Na_2SO_3 + S = Na_2S_2O_3$$

Commercially, it is prepared by passing sulphur dioxide into an alkaline solution of sodium sulphide, or by boiling sodium hydroxide with sulphur and passing in sulphur dioxide until the yellow colour of the solution is destroyed—

$$6NaOH + 4S = Na_2S_2O_3 + 2Na_2S + 3H_2O$$

$$Na_2S + 4S = Na_2S_5 \text{ (yellow)}$$

$$2Na_2S + 4SO_2 + 2NaOH = 3Na_2S_2O_3 + H_2O$$

It is used commercially as an antichlor to remove any free chlorine remaining in the material after bleaching with this gas—

$$4Cl_2 + 5H_2O + Na_2S_2O_3 = Na_2SO_4 + H_2SO_4 + 8HCl$$

It reacts also with iodine to form sodium tetrathionate and this reaction is used in iodimetric methods of volumetric analysis. Note, that the oxidation is more complete with chlorine—

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

It finds considerable use in photographic "fixing" solutions to remove any remaining silver halides—

$$2AgCl + 3Na_2S_2O_3 = Na_4[Ag_2(S_2O_3)_3] + 2NaCl$$

Crystals of sodium thiosulphate have the formula $Na_2S_2O_3 \cdot 5H_2O$. If the crystals are heated in a clean test-tube, the crystals melt to form a clear solution. If the mouth of the test-tube is loosely plugged with cotton wool to prevent the ingress of dust, no crystallization occurs on carefully cooling—the resulting solution is in fact *supersaturated*. If now a small fragment of a hypo crystal be added, crystallization occurs very rapidly, and the solution solidifies. If the solid is heated to decomposition it forms sodium sulphate and sodium pentasulphide—

$$4Na_2S_2O_3 = Na_2S_5 + 3Na_2SO_4$$

Pyrosulphuric Acid, $H_2S_2O_7$, is formed by the solution of sulphur trioxide in concentrated sulphuric acid, and is thus one of the oleums. It is a viscous oily liquid, fuming in air due to escape of some sulphur trioxide, and is known also as fuming or Nordhausen sulphuric acid. The acid or salts are also prepared by strongly heating ferrous sulphate crystals, or acid sulphates (*see* p. 759).

Persulphuric Acid, $H_2S_2O_8$, is known only in dilute solutions. It may be prepared by the electrolysis of fairly concentrated sulphuric acid, by the action of strong hydrogen peroxide on sulphuric acid, or by the solution of sulphur heptoxide in water—

$$\text{Electrolysis} \begin{cases} \text{Ionization } H_2SO_4 = H^+ + HSO_4^- \\ \text{Anode reaction } 2HSO_4^- \rightarrow 2(HSO_4) \rightarrow H_2S_2O_8 \end{cases}$$

$$\text{Hydrogen peroxide} \begin{cases} H_2SO_4 + H_2O_2 = H_2O + H_2SO_5 \\ 2H_2SO_4 + H_2O_2 = 2H_2O + H_2S_2O_8 \end{cases}$$

$$\text{Sulphur heptoxide } S_2O_7 + H_2O = H_2S_2O_8$$

Solutions of persulphuric acid decompose to liberate oxygen, via the intermediate formation of permonosulphuric acid (Caro's acid) and hydrogen peroxide—

$$H_2S_2O_8 + H_2O = H_2SO_4 + H_2SO_5$$
$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2$$
$$2H_2O_2 = 2H_2O + O_2$$

Modern methods for the manufacture of hydrogen peroxide involve the distillation of persulphuric acid solutions under reduced pressure.

Persulphates. When concentrated solutions of potassium hydrogen sulphate are electrolyzed at high current density (e.g. using point anodes), persulphuric acid is formed at the anode. This acid then reacts with the excess potassium hydrogen sulphate present, to precipitate potassium persulphate.

$$H_2S_2O_8 + 2KHSO_4 = K_2S_2O_8 \downarrow + 2H_2SO_4$$

The above formation of persulphuric acid presumably results from the effect of the concentration on the ionization of the potassium hydrogen sulphate—

$$KHSO_4 = K^+ + HSO_4^-$$

By the use of point anodes, the (HSO_4) radicals produced by neutralization of the bisulphate ions are brought into close contact to form persulphuric acid—

$$2(HSO_4) = H_2S_2O_8$$

Both persulphuric acid and the persulphates are oxidizing agents; thus,

they liberate iodine slowly from potassium iodide solutions, oxidize ferrous salts to ferric, and dissolve zinc without liberating hydrogen—

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2$$

$$2FeSO_4 + K_2S_2O_8 = Fe_2(SO_4)_3 + K_2SO_4$$

$$Zn + K_2S_2O_8 = ZnSO_4 + K_2SO_4$$

Manganese, cobalt, nickel and lead salts are oxidized, in presence of alkali, to their peroxides—

$$Mn(OH)_2 + K_2S_2O_8 = 2KHSO_4 + MnO_2$$

and silver nitrate reacts with potassium persulphate (but not with ammonium persulphate) to form a black precipitate of silver peroxide—

$$2AgNO_3 + K_2S_2O_8 + 2H_2O = 2KHSO_4 + 2HNO_3 + Ag_2O_2 \downarrow$$

Polythionic Acids, $H_2S_xO_6$, where x may be 2, 3, 4, 5, or 6.

If sulphuretted hydrogen is passed slowly through a solution of sulphur dioxide, colloidal sulphur is precipitated, and the milky liquid, known as Wackenroder's solution contains tetrathionic acid, pentathionic acid and a trace of trithionic acids. Dithionic and hexathionic acids are also known, and some of their salts are well known. Thus the reaction of iodine with sodium thiosulphate produces a colourless solution of sodium tetrathionate $Na_2S_4O_6$.

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

Halogen Compounds of Sulphur

Sulphur hexafluoride, SF_6, is formed when sulphur burns spontaneously in fluorine. It is a very stable colourless gas, its stability being in direct contrast with that of the other halogen compounds.

Sulphur monochloride, S_2Cl_2, is obtained as a yellow liquid by passing dry chlorine over sulphur fused in a retort. It has a pungent odour, and fumes in moist air due to hydrolysis—

$$2S_2Cl_2 + 3H_2O = 4HCl + H_2SO_3 + 3S$$

It will dissolve sulphur, iodine and certain halides and is used commercially in the vulcanization of rubber.

Sulphur dichloride, SCl_2, and sulphur tetrachloride, SCl_4 are also known. Sulphur monobromide, S_2Br_2, is obtained on heating sulphur with bromine in a sealed tube.

No sulphides of iodine have been reported.

Oxy-halogen Compounds of Sulphur. The most important of these include thionyl chloride, $SOCl_2$, chlorosulphonic acid, $Cl \cdot SO_2OH$, and sulphuryl chloride, SO_2Cl_2.

Thionyl chloride may be prepared by the action of sulphur dioxide on phosphorus pentachloride in the absence of moisture—

$$PCl_5 + SO_2 = POCl_3 + SOCl_2$$

The lower-boiling thionyl chloride (78° cf. 107°C) may then be separated by distillation. It is immediately hydrolyzed by water—

$$SOCl_2 + 2H_2O = 2HCl + H_2SO_3$$

Chlorosulphonic acid may be prepared by the action of hydrogen chloride gas on sulphur trioxide, again under moisture free conditions, since it is immediately hydrolyzed by water—

$$Cl\,.\,SO_2OH + H_2O = H_2SO_4 + HCl$$

Sulphuryl chloride has already been described in connexion with sulphur dioxide. It is a colourless liquid, readily decomposed by water—

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

CHROMIUM

Occurrence. The only ore of chromium having any importance is *chromite* (chrome iron ore), $FeO\,.\,Cr_2O_3$. Although theoretically this ore contains 68 per cent Cr_2O_3 with 32 per cent FeO, impurities are almost invariably present and the commercial ore seldom contains more than 50 per cent Cr_2O_3. In chromite as occurring in nature, the FeO is often replaced by MgO, and Cr_2O_3 by Al_2O_3 or Fe_2O_3. Consequently the formula for chromite is sometimes written as $(Fe, Mg)O\,.\,(Cr, Al, Fe)_2O_3$. Chromite is often assessed on the basis of its chromium-iron ratio, thus a pure chromite will have a chromium-iron ratio of 1·87:1.

The chief chromite producing countries are Turkey, Southern Rhodesia, the Union of South Africa, and the U.S.S.R.

Chromite is classified into three main groups according to the needs of industry—

(*a*) Metallurgical chromite, as used for the manufacture of ferrochrome, should have a content of not less than 48 per cent Cr_2O_3, with maxima of 1·25 per cent silica, 0·5 per cent sulphur, and 0·2 per cent phosphorus.

(*b*) Refractory chromite need not have so high a minimum Cr_2O_3 content as metallurgical chromite. The ore should, however, be uniform in respect of Cr_2O_3 content; high alumina and magnesia and low silica and iron contents are usually specified. A typical refractory chromite carries approximately 33 per cent Cr_2O_3, 30 per cent Al_2O_3, 17 per cent MgO, 15 per cent FeO, and as little as 2 per cent SiO_2.

(*c*) Chemical chromite should have a content of at least 48 per cent Cr_2O_3 with maxima of silica, sulphur and phosphorus similar to those imposed upon metallurgical chromite.

Extraction. Chromium is manufactured on a commercial scale by the following processes.

(i) *The Goldschmidt process* which is an alumino-thermic reaction in which chromic oxide, Cr_2O_3, is mixed with powdered aluminium and the whole fired by means of a previously ignited primer of magnesium ribbon inserted in sodium or barium peroxide. The main reduction reaction is as follows—

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3 + 112\,000 \text{ cal.}$$

The reduced chromium melts and collects in the lower portion of the reduction vessel from whence it is recovered after cooling. The chromium content of material produced by the Goldschmidt Process varies from 98–99 per cent metal.

(ii) *The Electrolytic process* in which an aqueous solution of chromic acid is electrolyzed gives rise to a very pure deposit of the metal. A typical electrolyte contains 250 g chromic acid and 2·5 g sulphuric acid per litre.

(iii) A very considerable proportion of the chromite mined is converted into ferrochrome by reduction with carbon in an electric arc furnace. The chromium content of ferrochrome varies from 66–72 per cent, whilst the carbon varies from 0·06–0·02 per cent in the case of low-carbon ferrochrome, to 4–8 per cent carbon in the case of high-carbon ferrochrome. A material known as Crom-X is also manufactured, this consists of ferrochrome mixed with ferrosilicon and sodium nitrate, the whole being pressed into briquettes. This material, like ferrochrome, is employed in the manufacture of low-alloy steels and irons.

Physical Properties of Chromium

(*a*) Chromium is a metal with a steel-grey colour which takes a brilliant polish.

(*b*) The hardness of chromium varies considerably according to the conditions of its preparation; for example, electrodeposited chromium exhibits a Brinell hardness of 800–900, whilst on annealing electrodeposited metal, a hardness of 80–100 Brinell is exhibited. If contaminated, chromium is intensely hard, and may only be cut and polished by the aid of diamond dust.

(*c*) Chromium is a heavy metal, density 7·14.

(*d*) Chromium exhibits a high melting point (1802°C), and a high boiling point (2482°C).

Chemical Properties of Chromium

(*a*) At atmospheric temperature chromium is stable in air, but when heated the metal burns to form the green chromic oxide, Cr_2O_3.

(*b*) Chromium dissolves readily in dilute hydrochloric acid or in dilute

sulphuric acid to give the corresponding chromous salts which are readily oxidized to the chromic salts.

Dilute nitric acid reacts with chromium to form chromic nitrate, but the concentrated acid renders chromium passive.

(*c*) Steam is decomposed by chromium at red heat, thus—

$$2Cr + 3H_2O = Cr_2O_3 + 3H_2 \uparrow$$

Uses of Chromium. Chromium has two chief uses, (i) for the manufacture of alloys, and (ii) for use as a protective coating.

Chromium alloys are outstanding for (*a*) high thermal and electrical resistance, (*b*) high tensile strength at elevated temperatures, (*c*) resistance to attack by many acids and alkalis, and (*d*) absence of deformation or deterioration at elevated temperatures up to 1100°C. Non-ferrous alloys containing approximately 80 per cent nickel and 20 per cent chromium find considerable application for the manufacture of electrical resistance elements and for items of furnace equipment such as annealing boxes, etc. Alloys of this series are manufactured under such trade names as "Nichrome," "Brightray," "Glowray" and "Pyromic." A similar alloy known as "Inconel" contains 80 per cent nickel, 13 per cent chromium, and 7 per cent iron. The alloy "Hastelloy C" containing a maximum of 20 per cent molybdenum, 18 per cent chromium, 6 per cent tungsten, and 7 per cent iron, with the balance of nickel is outstanding for its ability to resist such corrosive media as nitric acid, aqueous solutions of chlorine, free chlorine, acetic, formic and sulphurous acids, and the oxidizing action of ferric and cupric salts.

Chromium is added to steels in contents of from 2–30 per cent. The 2 per cent chromium steels are used for purposes where a high hardness is required. Chromium is often present to the extent of about 1–2 per cent in conjunction with nickel; these so-called nickel-chromium steels are of outstanding importance as alloy structural steels where a combination of high strength and resistance to shock are required. Chromium to the extent of 12·5–15 per cent is present in the "martensitic" stainless steels and the stainless irons, the former differing from the latter in that these stainless steels have a higher carbon content than the stainless irons (0·3 per cent as against 0·1 per cent). The "austenitic" stainless steels contain a higher chromium content, 18–30 per cent in conjunction with a nickel content of 8–20 per cent.

Chromium is also an important constituent in many cutting materials used in the form of tools such as high-speed steel, an alloy containing approximately 18 per cent tungsten, 4 per cent chromium, and 1 per cent vanadium, the balance being iron.

Electrodeposited chromium is a very hard metal with a characteristically bluish-white appearance and showing a very high resistance to tarnishing. In metal-finishing practice a very thin electrodeposit (0·00001 in. to

0·00005 in.) provides the necessary non-tarnishing properties. The electrolyte employed contains 250 g chromic acid and 2·5 g sulphuric acid per litre. A temperature of 50°–60°C is usually employed and a current density of 200–250 amperes per square foot; inert lead anodes are used.

Very much heavier deposits of chromium are applied to certain engineering components such as inspection gauges and various types of tools with the object either of improving the resistance to wear or imparting low frictional properties. These heavy deposits of chromium are often referred to as "hard" chromium deposits but it should be noted that such electrodeposits are no harder than the thinner coatings, nor are the methods of deposition different from those applied for the purpose of increasing corrosion resistance.

The chief valency states of chromium are two, three and six giving rise to chromous compounds, chromic compounds and compounds of hexavalent chromium respectively.

Chromous Compounds

Chromous Oxide, CrO, is a black oxide formed when chromium amalgam is exposed to the air.

Chromous Hydroxide, $Cr(OH)_2$, is formed as a yellow precipitate when an alkali hydroxide solution is allowed to react with the solution of a chromous salt. On reaction with acids chromous hydroxide forms blue solutions of the corresponding chromous salts. When heated, chromous hydroxide yields chromic oxide, water and hydrogen—

$$2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2\uparrow$$

Chromous salts are either blue in colour or alternatively form blue solutions and are powerful reducing agents, being more powerful in this respect than ferrous salts. On exposure to the atmosphere chromous salts are readily oxidized to the corresponding chromic salts.

Chromous Chloride, $CrCl_2$, may be prepared in the anhydrous state by the action of hydrogen chloride on heated chromium, or alternatively by reducing chromic chloride with hydrogen. Anhydrous chromous chloride is a white crystalline compound. The anhydrous salt forms a blue solution when it dissolves in water; from this solution crystals of the tetrahydrate, $CrCl_2 . 4H_2O$ may be obtained on evaporation. Alternatively, a solution of chromous chloride may be prepared by reduction of a solution either of a chromate, or of a chromic salt by means of zinc and hydrochloric acid.

Chromous Sulphate, $CrSO_4$, may be prepared by the action of sulphuric acid upon metallic chromium; from the solution thus produced blue crystals of the heptahydrate, $CrSO_4 . 7H_2O$, may be obtained.

Chromic Compounds

Chromic Oxide (Chromium Sesquioxide) Cr_2O_3, the most stable of the oxides of chromium is formed when either chromous oxide or chromium trioxide are heated in the air. It is also formed if chromic hydroxide is heated, or if ammonium dichromate is heated—

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2\uparrow + 4H_2O \quad . \quad . \ (a)$$

Alternatively, it is produced if a mixture of ammonium chloride and potassium dichromate is heated—

$$K_2Cr_2O_7 + 2NH_4Cl = Cr_2O_3 + N_2\uparrow + 4H_2O + 2KCl \quad . \ (b)$$

Reactions (*a*) and (*b*) involve reduction of the dichromate ion by the ammonium ion.

Chromic oxide is a green powder of high chemical stability; thus it cannot be reduced by heating with hydrogen or with carbon monoxide. It is insoluble in water and is a basic oxide which reacts with acids to form the corresponding chromic salts; it should be noted here that chromic oxide which has been calcined only dissolves in acids with difficulty. When fused with alkalis it forms chromites, thus—

$$Cr_2O_3 + 2KOH = 2KCrO_2 + H_2O$$

On the other hand, in the presence of oxidizing agents, chromic oxide forms a chromate when fused with alkalis—

$$2Cr_2O_3 + 8KOH + 3O_2 = 4K_2CrO_4 + 4H_2O$$

from oxidizing agent

Chromic oxide is thus an amphoteric oxide. In industry, chromic oxide finds considerable application as a pigment, and as an abrasive.

Chromic Hydroxide, $Cr(OH)_3$, is formed as a greenish-blue precipitate when ammonium hydroxide or an alkali hydroxide is added to the aqueous solution of a green chromic salt; if a violet chromic salt is employed another variety, probably a hydrated form, is produced. In the freshly-precipitated form chromic hydroxide reacts readily with acids, it also reacts with excess alkali hydroxide solution to form a green solution possibly either of colloidal chromium hydroxide, or alternatively of alkali metal chromite. Chromic hydroxide is a very weak base since it is precipitated along with ferric hydroxide and aluminium hydroxide by ammonium hydroxide in the presence of ammonium chloride.

Most of the chromic salts occur in two forms—a green form and a violet form; these differing colours are due to the formation of different stable complexes.

Chromic Chloride, $CrCl_3$, may be prepared in the anhydrous state either by heating metallic chromium in an atmosphere of chlorine, or alternatively

by heating a mixture of chromic oxide and carbon to redness in an atmosphere of chlorine—

$$Cr_2O_3 + 3C + 3Cl_2 = 2CrCl_3 + 3CO \uparrow$$

Chromic chloride may also be obtained in the anhydrous state by the action of sulphur chloride on chromic oxide, thus—

$$2Cr_2O_3 + 6S_2Cl_2 = 4CrCl_3 + 3SO_2 \uparrow + 9S$$

Anhydrous chromic chloride is a reddish-violet crystalline solid which only dissolves in water with great difficulty.

In the hydrated form chromic chloride may exist in several forms, varying in colour from violet to green; the solutions of these hydrated forms exhibit similar colours to the solid salts. These differing colours are due to the formation of stable complex ions, thus—

$[Cr(H_2O)_6]^{+++}$	Violet colour
$[Cr(H_2O)_5Cl]^{++}$	Green colour
$[Cr(H_2O)_4Cl_2]^{+}$	Green colour

It should be noted that in each of these complex ions there are six groups (water molecules or chloride ion) attached to the chromium ion.

Chromic Sulphate, $Cr_2(SO_4)_3 . 18H_2O$, is obtained in the form of violet crystals by the action of cold concentrated sulphuric acid on chromic hydroxide and evaporation of the resulting solution.

Chrome Alum or potassium chromium alum is prepared by the reduction of potassium dichromate solution, acidified with sulphuric acid, by means of sulphur dioxide—

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

On crystallizing the resulting solution crystals of chrome alum, $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$ separate out in the form of violet octahedra. Chrome alum finds considerable application as a mordant in the dyeing industry and for the tanning of leather.

Compounds of Hexavalent Chromium

Chromium Trioxide (Chromic Anhydride) CrO_3, is obtained in the form of dark red needles when concentrated sulphuric acid is added to a cold saturated solution of potassium dichromate.

$$H_2SO_4 + K_2Cr_2O_7 = K_2SO_4 + H_2O + 2CrO_3$$

The crystals of chromium trioxide may be separated by decantation, washed with concentrated nitric acid to remove sulphates and sulphuric acid, and finally dried on a porous plate in a current of warm air.

When heated, chromium trioxide melts at 196°C, and at 250°C decomposes to yield chromic oxide and oxygen—

$$4CrO_3 = 2Cr_2O_3 + 3O_2 \uparrow$$

Chromium trioxide is a powerful oxidizing agent; thus carbon is oxidized to carbon dioxide. If ethyl alcohol is dropped on to the oxide it takes fire with the formation of acetic acid and acetaldehyde.

Chromic oxide is very soluble in water yielding an acid solution containing dichromic acid, $H_2Cr_2O_7$, and possibly small contents of chromic acid, H_2CrO_4.

Chromates

Chromic Acid, H_2CrO_4, has not been isolated, but a large number of salts of this acid are known. For convenience they may be divided into (*a*) soluble chromates, and (*b*) insoluble chromates. The chromates are often isomorphous with the corresponding sulphates.

Sodium Chromate, Na_2CrO_4, probably the most important of all the soluble chromates, is manufactured to a large extent as the first stage in the production of many other chromium chemicals by roasting a mixture of pulverized chrome ore, soda ash and lime in an oxidizing atmosphere. The lime serves to avoid fusion of the mix.

$$4[Cr_2O_3 \,.\, FeO] + 8Na_2CO_3 + 7O_2 = 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2 \uparrow$$

The roasted mix is leached with hot water and the liquor concentrated, and sodium chromate is separated by direct crystallization.

In the laboratory sodium chromate may be prepared by the addition of an alkali to the solution of sodium dichromate, the reactions involved being depicted ionically as follows—

$$Cr_2O_7'' + 2OH' \rightleftharpoons 2CrO_4'' + H_2O \quad . \quad . \quad . \quad (a)$$

$$Cr_2O_7'' + CO_3'' \rightleftharpoons 2CrO_4'' + CO_2 \quad . \quad . \quad . \quad (b)$$

Sodium chromate occurs in the form of deliquescent, yellow crystals.

Potassium Chromate, K_2CrO_4, is also a yellow crystalline solid; it is however non-hygroscopic. It is prepared by using potassium carbonate instead of soda ash in the process described above. Potassium chromate is employed in volumetric analysis as an indicator (in silver nitrate titrations), in the manufacture of inks, in the manufacture of certain ceramic and glass colours, and in the manufacture of flux and metal-coating compounds such as welding electrodes.

Insoluble chromates are prepared by the addition of a soluble chromate, such as potassium or sodium chromate to the solution of a salt of a metal whose insoluble chromate is desired. Typical insoluble chromates include *barium chromate*, $BaCrO_4$, which is yellow, *strontium chromate*, $SrCrO_4$, also yellow, *lead chromate*, $PbCrO_4$ also yellow and often termed *chrome*

yellow; when treated with sodium hydroxide lead chromate yields *basic lead chromate*, $PbCrO_4 . PbO$, a pigment known as *chrome red*. *Silver chromate*, Ag_2CrO_4, is brick-red in colour.

Dichromates. Sodium chromate manufactured as described above from chrome ore, soda ash and lime, is treated with sulphuric acid whilst in aqueous solution; on evaporation sodium sulphate crystallizes first and on further evaporation *sodium dichromate dihydrate* separates out.

$$2Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_2O_7 + H_2O$$

Potassium Dichromate, $K_2Cr_2O_7$, is prepared by adding potassium chloride to an aqueous solution of sodium dichromate when the potassium salt, being only slightly soluble, separates out in the form of anhydrous orange-red crystals.

For many purposes, on account of its lower cost and higher solubility in water, sodium dichromate is preferred to potassium dichromate. These two dichromates resemble one another closely in their chemical properties. Sodium dichromate is employed in the manufacture of pigments, for producing corrosion-resisting films on magnesium-base light alloys, and for colouring copper-base alloys such as brasses.

Potassium dichromate is used in the manufacture of certain types of blue print paper, in photographic processing and in certain specialized textile and tanning processes. In the laboratory potassium dichromate is employed in volumetric analysis as an oxidizing agent; in acid solution, one molecule of the salt will provide three atoms (i.e. six equivalents) of oxygen—

$$2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 6\overline{O} + 8H_2O$$

Thus, one molecule of potassium dichromate will oxidize six atoms (i.e. six equivalents) of ferrous iron—

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

In a similar manner, potassium dichromate will oxidize halides quantitatively to the corresponding halogens as shown by the following typical equation—

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI = 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

Potassium dichromate is also employed as a volumetric oxidizing agent in chemical analysis to oxidize quantitatively ferrous salts to ferric salts, sulphurous acid to sulphuric acid, etc.

When heated to high temperatures sodium and potassium dichromates decompose as follows—

$$4Na_2Cr_2O_7 = 4Na_2CrO_4 + 2Cr_2O_3 + 3O_2 \uparrow$$

In aqueous solution, the addition of an alkali results in the formation of the corresponding chromate, thus—

$$Cr_2O_7'' + 2OH' \rightleftharpoons 2CrO_4'' + H_2O$$

Chromyl Chloride, CrO_2Cl_2, is prepared by the action of concentrated hydrochloric acid and concentrated sulphuric acid on an aqueous solution of chromic acid; the mixture is cooled and after standing, the lower layer of chromyl chloride is run off by means of a tap funnel.

Chromyl chloride is a dark red liquid, boiling at 116°C. It is hydrolyzed in aqueous solution to form chromic and hydrochloric acids. It is therefore possible to use these facts as a means of detecting the presence of chlorides in the presence of bromides and iodides since neither of these two latter groups of compounds form compounds comparable to chromyl chloride.

To carry out a test to detect the presence of a chloride, the suspected substance is heated with potassium dichromate and concentrated sulphuric acid; if a chloride is present, chromyl chloride is formed which distils over and reacts with water to form a solution of chromic acid. This is readily detected by adding an aqueous solution of lead acetate when an insoluble yellow precipitate of lead chromate is formed. The sulphuric acid fulfils two purposes, (*a*) to react with the suspected substance to yield the hydrogen chloride—on the presumption that a chloride is present, and (*b*) to react with potassium dichromate to yield chromium trioxide which reacts with the hydrogen chloride to form chromyl chloride.

CHAPTER 25

THE ELEMENTS OF GROUP VII

THE elements of Group VII fall into two sub-groups—A, the halogens, and B, manganese, technitium and rhenium.

Fluorine—Chlorine	Manganese—Technitium—Rhenium	VIIA
	Bromine—Iodine	VIIB

Little is known, as yet, about the chemistry of technitium and rhenium, and there appears little resemblance between manganese and the halogens apart from the formation of permanganates which are isomorphous with the perchlorates. Permanganic and perchloric acid are both monobasic and powerful oxidizing agents.

THE HALOGENS

The elements fluorine, chlorine, bromine and iodine are known collectively as the *halogens*, a term coined by Berzelius in 1825 to describe their property of forming salts by direct combination with most metals. They are non-metallic elements, although the hydroxy-compounds of iodine are rather more basic than acidic.

The expected decrease in volatility occurs with increase in molecular weight; thus, fluorine and chlorine are both gases at ordinary temperatures, bromine is liquid and iodine is solid.

Halogen	Symbol	State	Atomic Weight	Melting Point	Boiling Point
Fluorine .	F	Pale yellow gas	19·00	− 223°C	− 187°C
Chlorine .	Cl	Greenish-yellow gas	35·46	− 102°C	− 34°C
Bromine .	Br	Reddish liquid	79·92	− 7°C	+ 59°C
Iodine .	I	Violet solid	126·92	+ 113°C	+ 184°C

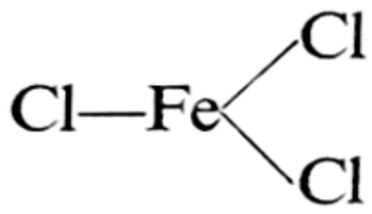
As a family the halogens are all univalent and form both covalent and electrovalent compounds. In the following table the electronic structure

of the halogens is compared with that of the inert gases which form the next group of the Periodic Table—

F	2	.	7						Ne	2	.	8					
Cl	2	.	8	.	7				A	2	.	8	.	8			
Br	2	.	8	.	18	.	7		Kr	2	.	8	.	18	.	8	.
I	2	.	8	.	18	.	18	. 7	Xe	2	.	8	.	18	.	18	. 8

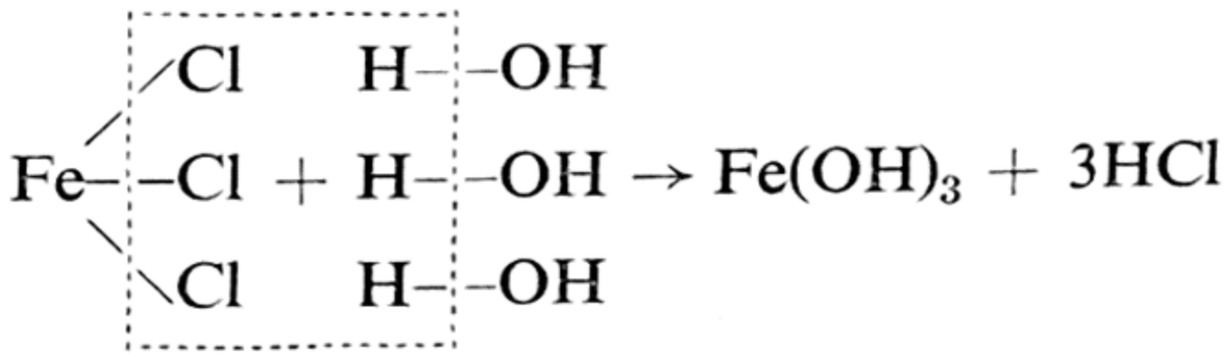
It will be noted that each halogen requires one additional electron in order to acquire the "inert-gas" structure. This additional electron may be acquired by one of two processes, namely, the formation of either a covalent or of an electrovalent linkage (*see* p. 68).

The molecules of the halogens are covalent and have the formulae F_2, Cl_2, Br_2 and I_2. Other examples of covalent halogen compounds include hydrogen chloride, HCl, and other halogen compounds of the non-metals such as carbon tetrachloride, CCl_4, and phosphorus trichloride PCl_3. Such compounds are usually gaseous or else liquids or solids with relatively low melting points and boiling points. On the other hand, the halides of the more electropositive metals are electrovalent (e.g. sodium chloride, potassium chloride, etc.). These are solids with high melting points and dissolve in water without hydrolysis. With the less electropositive metals (Fe, Sn, Pb, etc.), the salt-like nature of the halides is less pronounced. Thus the compounds $FeCl_3$, $SnCl_4$, and $PbCl_4$ are either solids or liquids with low boiling points, properties which suggest that they are mainly covalent, e.g.



In the presence of water these compounds ionize, often with appreciable hydrolysis—

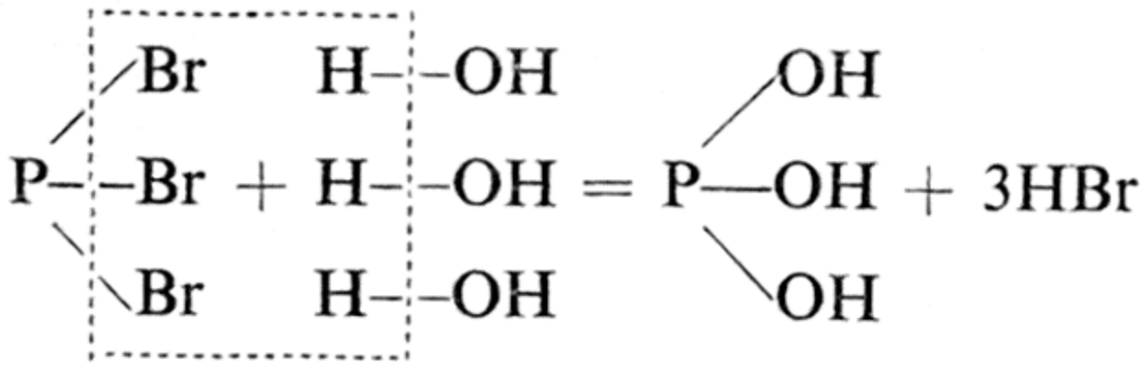
Ionization $\quad FeCl_3 = Fe^{+++} + 3Cl^-$



The insoluble halides, such as silver chloride and mercurous chloride, are mainly covalent, Ag—Cl and Cl—Hg—Hg—Cl.

The covalent nature of the halogen compounds of the non-metals is revealed by their low melting points and boiling points. They are usually

more or less rapidly hydrolyzed by water and fume in moist air due to the liberation of the hydrogen halide—

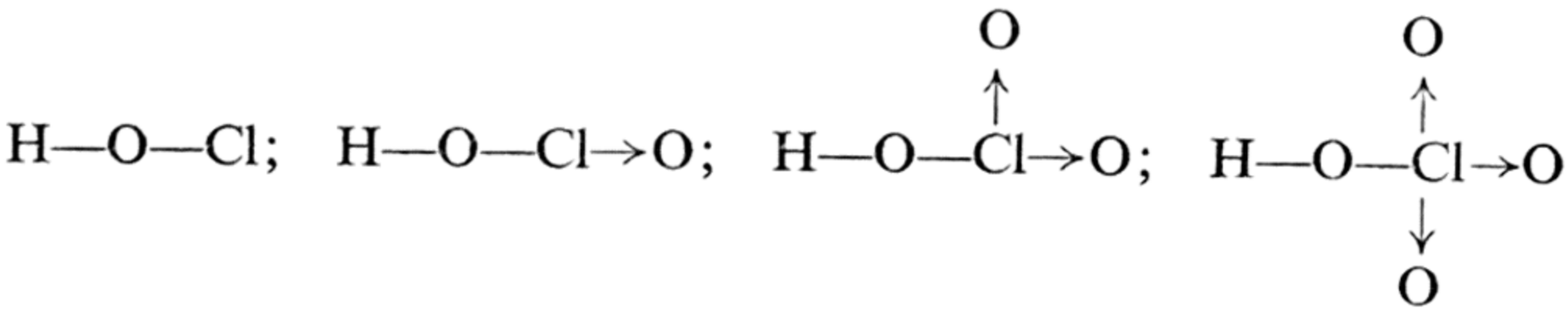


(that is, $PBr_3 + 3H_2O = H_3PO_3 + 3HBr$)

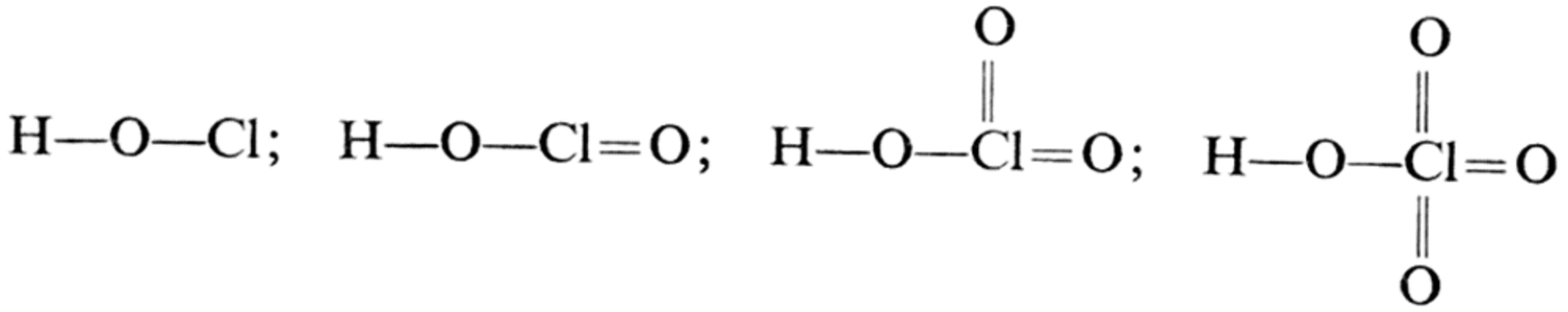
This reaction will be referred to later in connexion with the laboratory method for preparing hydrogen bromide and hydrogen iodide. Not all the halogen compounds of the non-metals are hydrolyzed by water, however, and the following exceptions should be carefully noted—

Not hydrolyzed by water—NF_3, CF_4, CCl_4, PF_5 and SF_6.

The oxy-compounds of the halogens were until very recently considered to have such formulae as—



with the additional oxygen atoms (after hypochlorous acid, HOCl) attached by co-ordinate links (*see* p. 75). It is now considered, however, as a result of the realization that the true co-ordinate linkage occurs much less frequently than was formerly supposed, that in these oxy-compounds the oxygen is linked by a normal double covalency bond, and the valency of the halogen increases in the order 1, 3, 5 and 7—



A similar increase in covalency occurs in certain interhalogen compounds, particularly those of iodine, such as ICl_3, IF_5, IF_7 and also I_2O_5.

Comparative Review of the Properties of the Halogens

1. Increase in atomic weight corresponds to a progressive change in physical properties—colour, melting and boiling points, odour, poisonous nature, and solubility.

2. General chemical reactivity decreases from fluorine to iodine. Fluorine is the most reactive element known, and chlorine, bromine and iodine show a progressive decrease in reactivity in this order.

3. Fluorine has such a high affinity for hydrogen that it will explode or otherwise react vigorously with compounds containing this element, e.g. water, hydrocarbons, etc. Chlorine reacts much less vigorously with such compounds, although under the right conditions of photo-chemical activation it will react explosively with hydrogen. The affinity for hydrogen decreases further with bromine and is least with iodine.

4. This decreasing reactivity for hydrogen is paralleled by a similar decreasing reactivity of the halogens, in the order fluorine to iodine, towards the metals.

5. The stability of the compounds formed with the non-metals increases, in general, from fluorine to iodine. In particular, the oxy-compounds of iodine are more stable than the oxy-compounds of the other halogens, but this may be due to a difference in the chemical nature of these compounds since the oxy-compounds of bromine are relatively few and unimportant. The most stable oxy-compounds of each halogen are those containing the most oxygen; thus perchloric acid, $HClO_4$, is much more stable than hypochlorous acid, HOCl.

6. In many of its properties iodine shows a more or less abrupt change as compared with those of the other halogens. This behaviour is explained by the fact that whereas fluorine is the most electro-negative of all the elements (with chlorine and bromine progressively less electronegative), iodine is predominantly electropositive in many of its compounds.

7. Fluorine is also anomalous in many of its properties when compared with the other halogens, and is in many respects similar to oxygen.

FLUORINE

Fluorine and the other halogens do not occur free in nature, a fact which indicates their high chemical reactivity. The principal minerals containing fluorine are *fluorspar* (or calcium fluoride) CaF_2, *cryolite* (or sodium aluminium fluoride) Na_3AlF_6, and *fluor-apatite* $CaF_2 . 3Ca_3(PO_4)_2$.

Preparation. The element was first isolated by Moissan in 1886 by the electrolysis of a solution of potassium fluoride (KF) in anhydrous hydrogen fluoride at −23°C. The electrolysis was carried out in a U-shaped platinium-iridium vessel as shown in the diagram opposite. The platinum-iridium electrodes were insulated from the cell by stoppers of fluorspar and on passing the current fluorine gas was evolved from the anode. The temperature of the cell was maintained in the region of −23°C by immersion in a bath of boiling methyl chloride (b. p. −23°C).

This method of preparing fluorine resulted only after numerous other methods had unsuccessfully been attempted.

(*a*) Electrolysis of hydrofluoric acid as the electrolyte fails because any fluorine liberated immediately reacts with the water present

$$2F_2 + 2H_2O = 4HF + O_2$$

Water *must* therefore be absent.

(*b*) Anhydrous HF (a liquid, b. p. 19·5°C) also fails as the electrolyte because it is a non-conductor of electricity.

(*c*) Electrolysis of fused fluorides, such as KF, fails because of the very high melting points of such compounds, and the very great reactivity of fluorine at such temperatures. Electrolysis of aqueous solutions of fluorides fails for the same reason as (*a*).

The problem was eventually solved, as described above, when it was discovered that although anhydrous hydrogen fluoride is a non-conductor it is a very good ionizing solvent (compare with water, which is a poor conductor but also a very good ionizing solvent), so that solutions, such as that used by Moissan, may be successfully electrolyzed. Since anhydrous HF

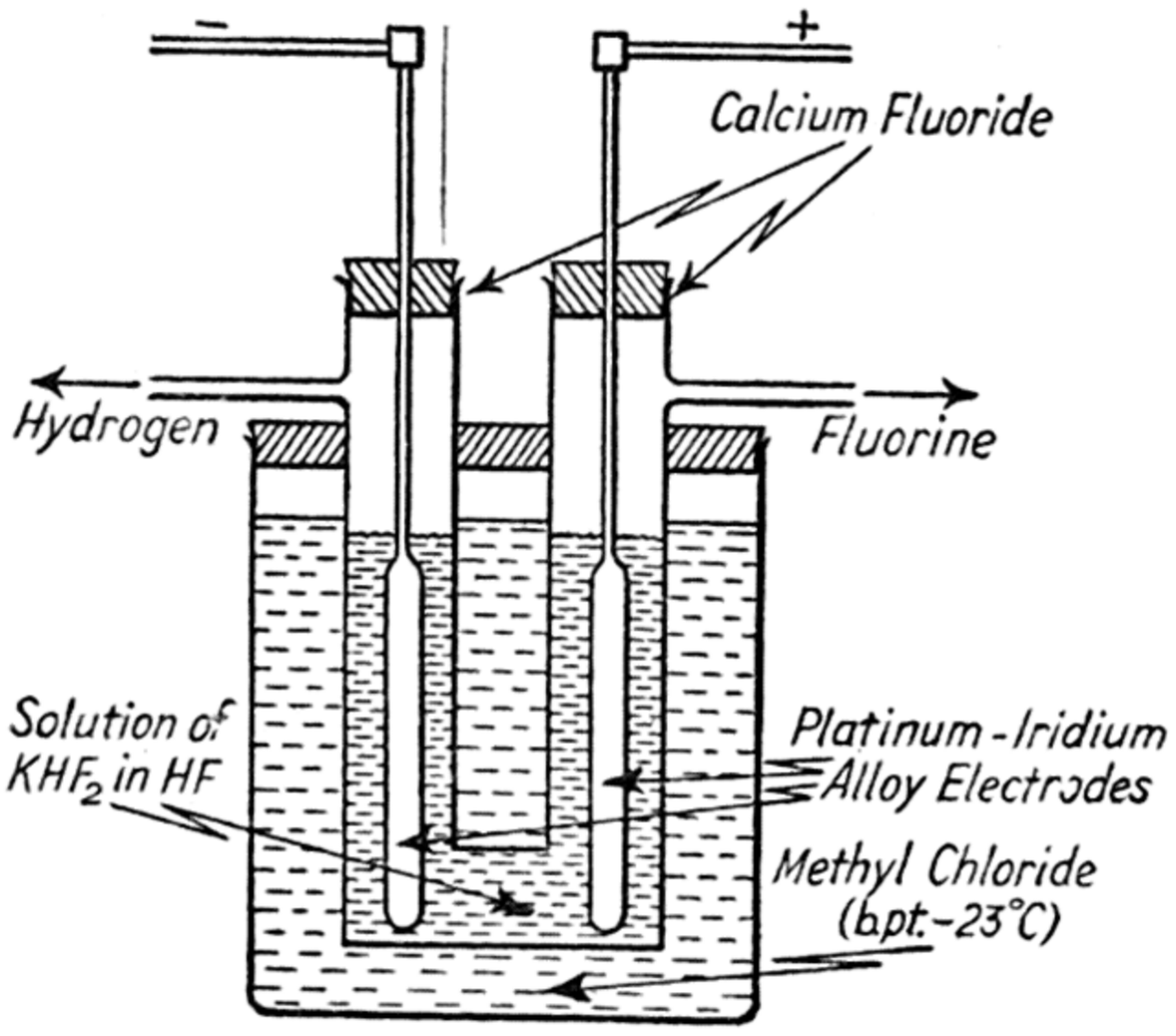


FIG. 237. Preparation of Fluorine

boils at about room temperatures (19·5°C), it became necessary to work at lower temperatures to reduce the loss of HF by evaporation. The use of methyl chloride resulted from the convenient boiling point of this liquid.

Considerable progress in the preparation of fluorine on a commercial scale was made during the second World War, principally in Germany and in the United States. Numerous processes have been described, differing mainly in the design of the electrolytic cell and in the composition of the electrolyte, so that no standard process can be described. In general, however, the cells are of the diaphragm type, with a metallic grid separating the anode and cathode compartments, and the electrolyte is a fused anhydrous hydro-fluoride, such as KF.2HF (in the cell operating at about 100°C) or KF.HF (in the higher temperature cells). Small amounts of lithium fluoride (LiF) (often less than 1 per cent) are added to the electrolyte to lower the melting point. The anodes consist of graphite

electrodes, often impregnated with metallic copper to improve their strength and chemical resistance, whilst the cathodes are usually of ordinary carbon steel. The cell is also of carbon steel, but where contact with fluorine occurs, Monel-metal or other nickel alloy is preferred.

It is absolutely necessary that the delivery pipes, and in fact all parts of the plant which come into contact with the very active fluorine, be kept free from moisture, oils, grease, and other hydrogen-containing compounds. Failure to observe this necessary precaution may result in the fluorine "burning" through the metal, sometimes producing flames of white hot intensity due to the combustion of the metal in the fluorine. The reaction of the fluorine, in the first instance, with such waste materials (oil, etc.) develops sufficient local heat to promote vigorous attack of the metal container with results as stated above.

Properties. Fluorine is a colourless gas in dilute concentrations, but, when concentrated, it has a greenish tinge and is more yellow than chlorine. It has a pronounced odour, when dilute resembling that of ozone, and is said to be detectable by smell to a few parts per million. Its melting and boiling points are $-233°C$ and $-188°C$ respectively.

Chemically, fluorine is the most reactive of all elements. It combines with practically every material under suitable conditions, and in most cases the reaction occurs spontaneously at ordinary temperatures. It does not however react with the inert gases, nor with compounds which are already fully combined with fluorine, such as CF_4 and the metallic fluorides, such as CaF_2, CuF_2, KF, etc.

Reaction of Fluorine with Hydrogen. The enormous affinity of fluorine for hydrogen is shown by such reactions as—

(*a*) Solid fluorine explodes violently with liquid hydrogen at $-253°C$

$$H_2 + F_2 = 2HF$$

(*b*) Fluorine reacts spontaneously and often violently with compounds containing hydrogen. Thus, vigorous reaction occurs with water—

$$2F_2 + 2H_2O = 4HF + O_2$$

Sometimes, however, water has been observed to accumulate in presence of fluorine, until suddenly the reaction occurs with explosive violence.

(*c*) The spontaneous reaction between fluorine and most organic compounds containing hydrogen has already been mentioned as one of the hazards encountered in the commercial manufacture of the gas.

Reaction of Fluorine with other Non-metals. These, with the exception of the inert gases, oxygen, nitrogen, and possibly chlorine, all react vigorously with fluorine even at ordinary temperatures. Mixtures of fluorides are usually formed (e.g. PF_3 and PF_5). The student should particularly note the ability of fluorine to form compounds in which the other element develops its maximum valency, e.g. PF_5, SF_6 (and OsF_8). Powdered

charcoal, phosphorus and sulphur are ignited by fluorine to form carbon tetrafluoride and mixtures of the sulphur and phosphorus fluorides respectively, the reaction with charcoal being particularly remarkable in view of the non-reactivity of the other halogens with this element.

Fluorine readily attacks both free and combined silicon (silicates, glass, etc.) to form silicon tetra-fluoride, SiF_4, but the reaction with glass is said not to occur if the fluorine is free from HF and the glass is dry. A novel method of detecting fluorine when present in quantity is to expose a piece of asbestos cord or glass wool to the gas. If these burst into flame, then the gas is fluorine. This high reactivity is also revealed by the fact that windows of laboratories in which work on fluorine is being carried out become uniformly frosted after a few weeks, although the atmosphere of the laboratory may itself be comparatively free from fluorine. It has been noted that fluorine has no action on dry glass, and this suggests that the etching action is due to the HF liberated by the action of fluorine on moisture present.

Boron ignites in fluorine to form boron trifluoride, BF_3, a colourless fuming gas, which reacts vigorously with water (*see* below).

Reaction of Fluorine with Metals. The reactive alkali and alkaline-earth metals ignite spontaneously in fluorine at ordinary temperatures, to form the corresponding fluorides, NaF, etc. With the less reactive metals (Fe, Cu, etc.) the reaction is comparatively slow at ordinary temperatures but becomes vigorous at higher temperatures. Sufficient heat is then liberated to make the reaction self-sustaining—that is, no further heating is necessary. The relatively greater resistance shown by nickel (and Monel metal), copper, magnesium and aluminium as compared with iron and steel is attributed to the protective action of the fluoride film (e.g. CuF_2) which quickly covers the exposed surface of the metal. In the case of iron and steel, the FeF_3 film is less protective and reaction occurs at less elevated temperatures, becoming vigorous and self sustaining at 400°C–500°C.

Uranium hexafluoride, UF_6, is especially interesting because it is the only uranium compound obtainable in the form of a gas. It is also one of the most reactive substances known; it reacts explosively with practically every organic compound.

Reaction of Fluorine with Organic Compounds. No organic compound, with the exception of CF_4 is completely resistant to fluorine. A small, but increasing, number of fluorine-substituted organic compounds are now manufactured commercially. These include the *freons*, a class of liquid compounds of the type CCl_2F_2, which are rapidly becoming important in refrigeration and air-conditioning plant. Their use permits considerable reduction in the size of the plant, and is not attended by the usual dangers associated with escape of ammonia or sulphur dioxide from the more conventional plant. *Teflon* is a thermoplastic fluocarbon in many ways

analogous to polythene produced by the high pressure polymerization of ethylene.

Ethylene (C_2H_4) polymerized → Polythene (Alkathene)

Tetrafluo-ethylene (C_2F_4) polymerized → Teflon

Teflon is relatively stable thermally and is quite inert to chemical reagents.

Compounds of Fluorine

Hydrogen Fluoride is prepared by the action of concentrated sulphuric acid on fluospar—

$$CaF_2 + H_2SO_4 = CaSO_4 \downarrow + 2HF$$

Glass apparatus cannot be used because it is attacked by the HF. The reaction is carried out instead in cast-iron retorts and the HF distillate absorbed in water contained in lead boxes. The aqueous solution, so produced, is usually stored in gutta-percha (rubber), lead or waxed bottles. The *anhydrous acid* is prepared by carefully heating the hydrofluoride KHF_2 (prepared by adding KF to the aqueous solution of HF and evaporating) to drive off moisture, followed by more vigorous heating to decompose the KHF_2 and liberate the HF.

$$KHF_2 = KF + HF$$

The liquid HF which distils over is then electrolyzed between platinum electrodes to remove the last traces of water, a reaction which becomes intelligible when it is remembered that anhydrous HF is a non-conductor. The anhydrous acid, unlike the aqueous acid, does not attack glass but does attack rubber. It is therefore stored in glass vessels.

Properties of Hydrogen Fluoride. Both the anhydrous and its aqueous solution should be treated with respect, since contact with the skin raises blisters, and the vapours if inhaled may have serious effects.

The anhydrous acid is a liquid at ordinary temperatures, the boiling point being 19·5°C. The aqueous solution, like the other halogen acids, forms a constant boiling mixture which in this case contains 37 per cent HF and boils at 120°C.

Concentrated aqueous solutions of HF behave as a *weak* monobasic acid, but the formula of the acid in solution is not HF but rather H_2F_2. The $[HF_2]^-$ ion found in such compounds as KHF_2 is thought to have the structure $[F—H..F]^-$ involving a so-called "hydrogen bond." Vapour density determinations of the *anhydrous acid* at ordinary temperatures indicates the structure to be predominantly H_3F_3, although more probably it is a mixture of H_2F_2, H_3F_3, H_4F_4 and H_5F_5, in which the highly polar HF molecules link themselves by dipolar forces rather than by definite valency bonds. There is no evidence that the valency of fluorine is ever other than one.

Action of H_2F_2 on Silica and Glass. Strong solutions of H_2F_2 readily attack silica to form the gas silicon tetra-fluoride, which reacts with excess of H_2F_2 to form hydrofluosilicic acid, H_2SiF_6. If heated the latter decomposes and the SiF_4 escapes.

$$SiO_2 + 2H_2F_2 = SiF_4\uparrow + 2H_2O$$
$$SiF_4 + H_2F_2 = H_2SiF_6$$

This reaction is the basis of the quantitative method for estimating silica, for example, in the analysis of minerals and ores. The loss in weight of the platinum crucible and contents after repeated heating with small quantities of H_2F_2 gives directly the weight of silica in the original sample.

The etching of glass is a similar reaction and if carried out at ordinary temperatures results in the formation of fluosilicates, for example—

$$CaSiO_3 + 3H_2F_2 = CaSiF_6 + 3H_2O$$

Silicon tetrafluoride is hydrolyzed by water to form silicofluoric acid and silicic acid—

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$$

Well known salts of silicofluoric acid include potassium silico-fluoride (or fluosilicate) K_2SiF_6 and also $PbSiF_6$.

Boron Trifluoride, BF_3, formed by the action of H_2F_2 on B_2O_3, shows, like SiF_4, a similar reactivity towards water—

$$4BF_3 + 3H_2O = 3HBF_4 + H_3BO_3$$

(HBF_4: fluoboric acid)

Oxides of Fluorine. The only oxide of fluorine known to be stable at room temperature is fluorine monoxide, F_2O. It is prepared together with oxygen and ozone by passing fluorine through a 2 per cent solution of sodium hydroxide—

$$2NaOH + F_2 = 2NaF + F_2O + H_2O$$

It is a colourless gas (b. p. $-146°C$,) which does not attack glass and is a powerful oxidizing agent.

Estimation of Fluorine. Fluorides are detected most simply by treating the solid with concentrated sulphuric acid and holding a wet glass rod in the liberated HF gas. If the glass rod becomes frosted, the presence of a fluoride is indicated.

Quantitatively, fluorine and fluorides are estimated by conversion into the insoluble CaF_2, or better the compound PbClF.

Uses of Fluorine. The commercial application of fluorine compounds is increasing rapidly at the present time, as a result of the successful commercial production of the gas. Examples of such applications include—

(*a*) The use of the freons in refrigeration and air-conditioning plant.

(*b*) The use of H_2F_2 and BF_3 in the petroleum industry as catalysts in the synthesis of high octane petrols by alkylation processes.

(*c*) The use of sulphur hexa-fluoride, SF_6, as an insulator in high-voltage and X-ray apparatus.

(*d*) Plastic fluocarbons, such as Teflon, analogous to, but much more stable thermally and resistant chemically than polythene.

(*e*) The use of compounds, such as ClF_3 in incendiary warfare—since relatively small quantities of such compounds may ignite petroleum, and other inflammable fluids.

Summary of Fluorine Chemistry

1. Most reactive element known. Valency is one. In all its reactions, fluorine is strongly exothermic.

2. Combines *directly* with nearly all elements and compounds, the principal exceptions being the inert gases, oxygen, CF_4 and other compounds fully combined with fluorine (CaF_2, SF_6, etc.).

3. Fluorine appears to have the exceptional power of exciting the highest valency of other elements. Thus PF_5 and SF_6 are both *very* stable and show no tendency to thermal dissociation; IF_5 and OsF_8 are stable to 400°C.

4. Extremely reactive towards hydrogen and hydrogen-containing compounds (water, hydrocarbons, etc.).

5. Forms fluo-compounds with the other halogens—

ClF_3 (b. p. 12°C)	BrF_3 (b. p. 127°C)	IF_5 (b. p. 97°C)
	BrF_5 (b. p. 40°C)	IF_7 (b. p. 5–6°C)

6. Most of the compounds of fluorine with non-metals fume in air and are immediately hydrolyzed by water—exceptions include NF_3, PF_5, CF_4, SF_6, whilst IF_7 is only slowly attacked.

7. Does not form oxy-compounds analogous to those of chlorine and the other halogens. F_2O is the only oxide stable at ordinary temperature.

8. Hydrogen fluoride—formula not simple. Aqueous acid is mainly H_2F_2, and is a *weak* acid. Attacks silica, glass, etc. The anhydrous acid, formula probably H_3F_3, is a liquid (b. p. 19·5°C). It is a non-conductor but is a good ionizing solvent.

9. AgF is soluble in water (AgCl, AgBr, AgI are all insoluble). CaF_2 is insoluble ($CaCl_2$ etc., are deliquescent soluble salts).

CHLORINE, BROMINE AND IODINE

The remaining halogens are sufficiently similar in their properties to justify discussing their chemistry together. It is hoped, by this treatment, that the student will be better able to appreciate this similarity in properties and, where differences do occur, to focus more easily on the reasons for

such differences. Unless specifically stated, the reactions discussed below for chlorine apply also to bromine and iodine.

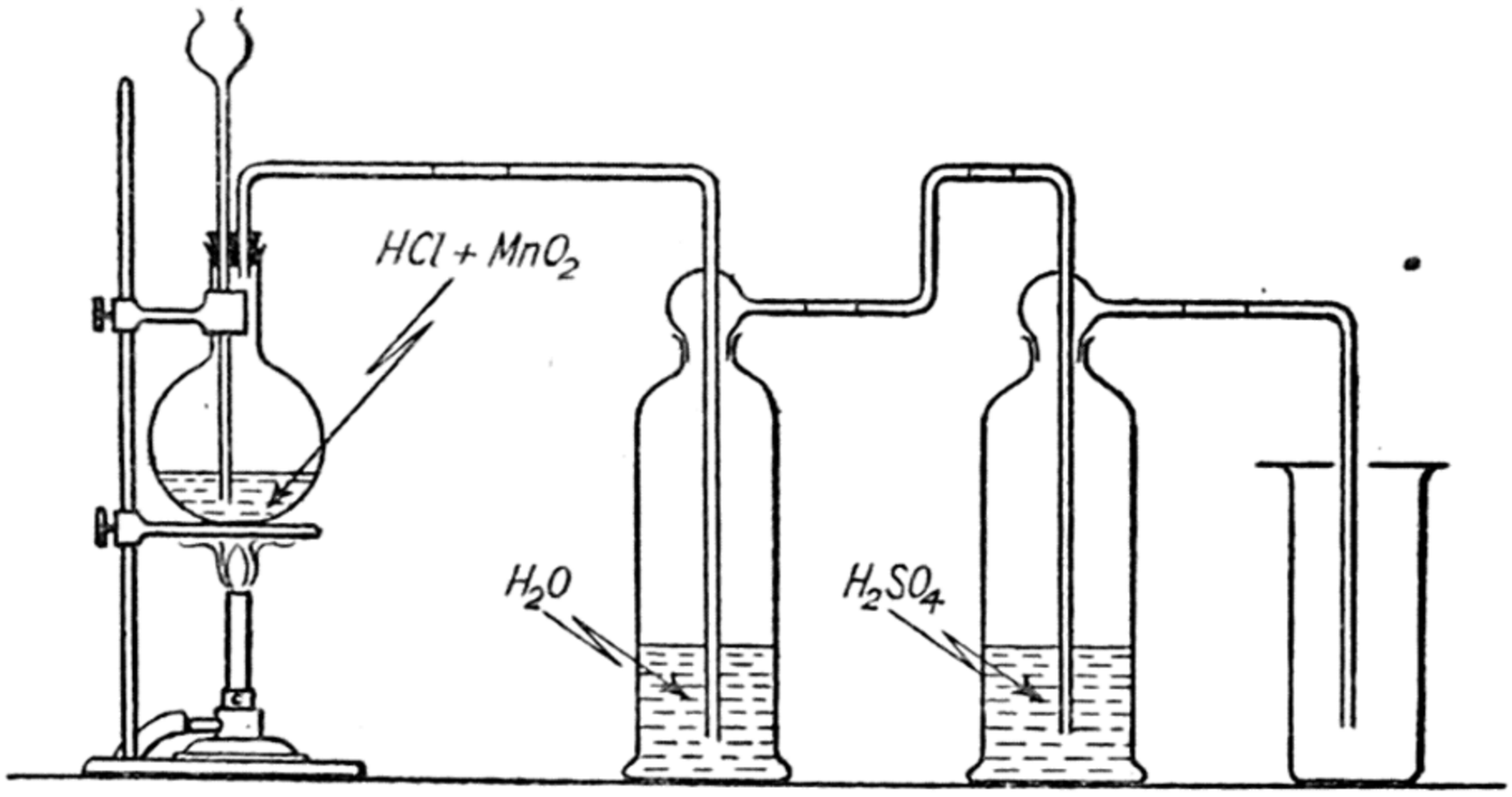


FIG. 238. Preparation of Chlorine

Occurrence. *Common Salt* (sodium chloride) NaCl, *Sylvine* (potassium chloride) KCl, *Carnallite* (potassium magnesium chloride)

$$KCl \cdot MgCl_2 \cdot 6H_2O$$

are a few of the more abundant compounds of chlorine which are found in nature. The Stassfurt deposits contain about 1 per cent of *magnesium*

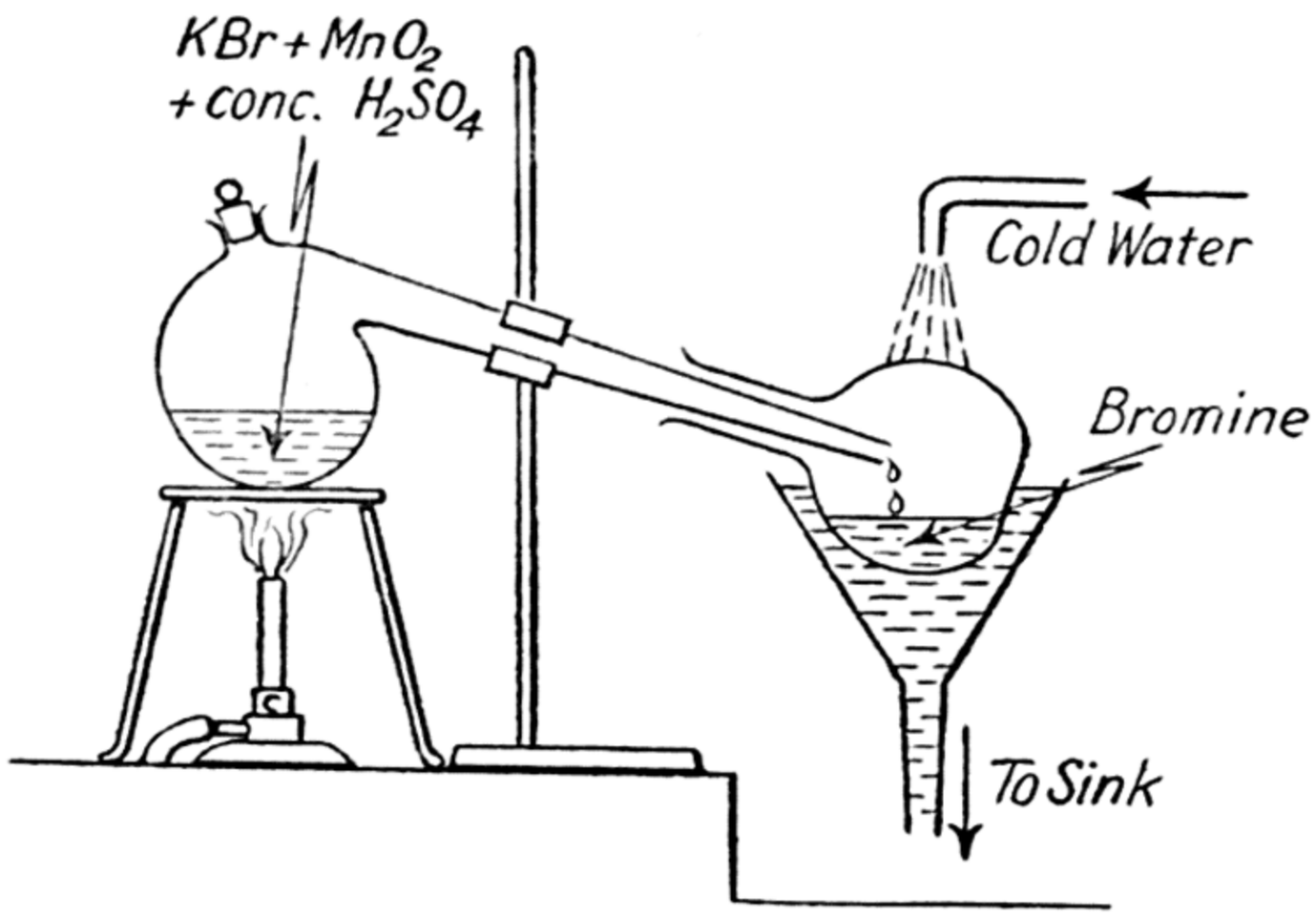


FIG. 239. Preparation of Bromine

bromide, smaller quantities of which occur in sea, mineral and spring waters. The Dead Sea contains about 9 per cent magnesium bromide. Like bromine, iodine compounds are widely distributed in nature. Thus small quantities occur in sea water, sea-weed, in oil-well brines, and also as the important *sodium iodate* in the Chile saltpetre deposits.

Preparation. The general method in the laboratory is to add concentrated sulphuric acid to a mixture of the halide and manganese dioxide and *heat*.

$$KCl + H_2SO_4 = KHSO_4 + HCl$$
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

Manganic chloride ($MnCl_3$) is formed as an unstable intermediate product but this decomposes to form manganous chloride and liberate chlorine. Chlorine, being a gas, is collected by upward displacement of air but may

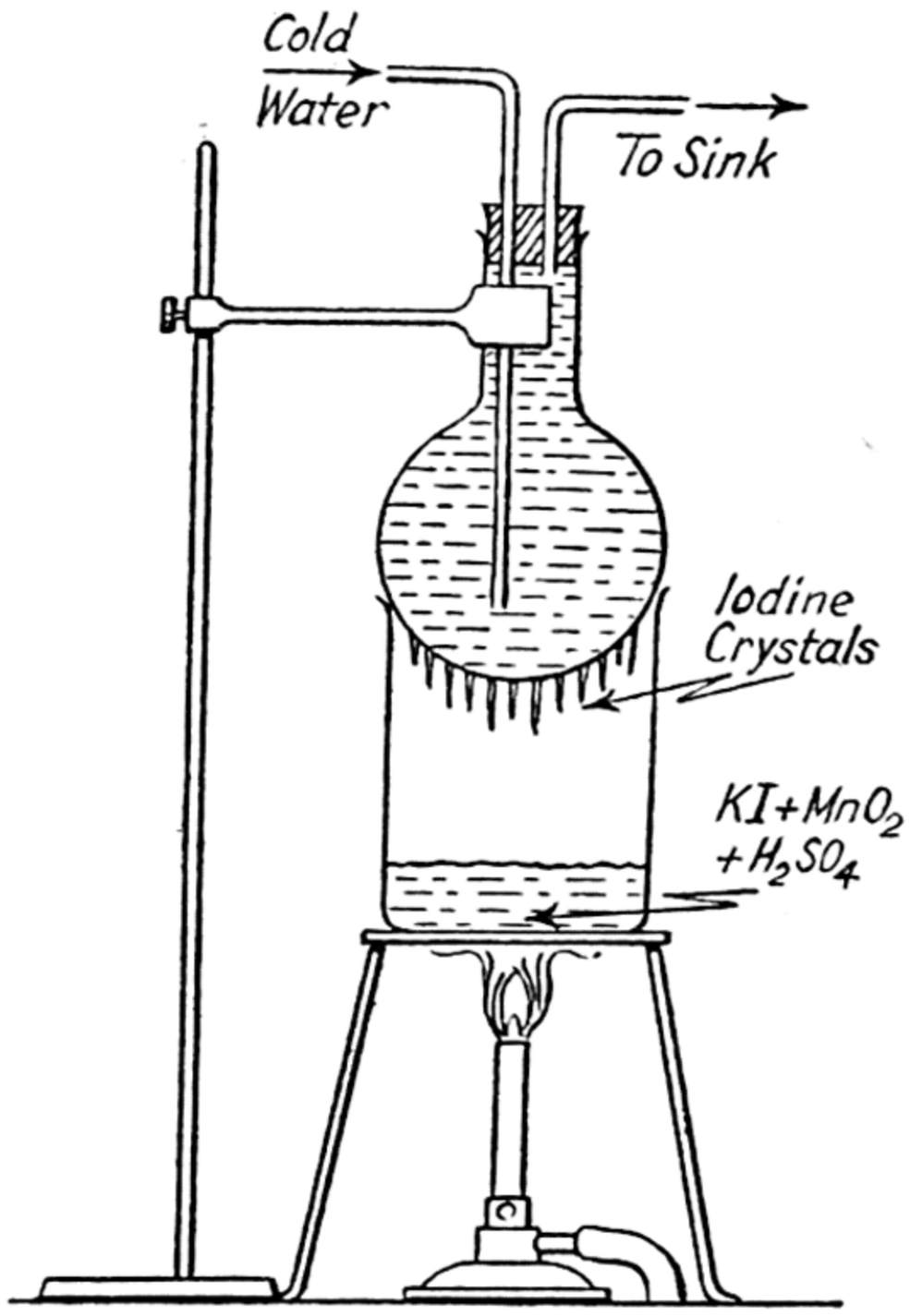


FIG. 240. Preparation of Iodine

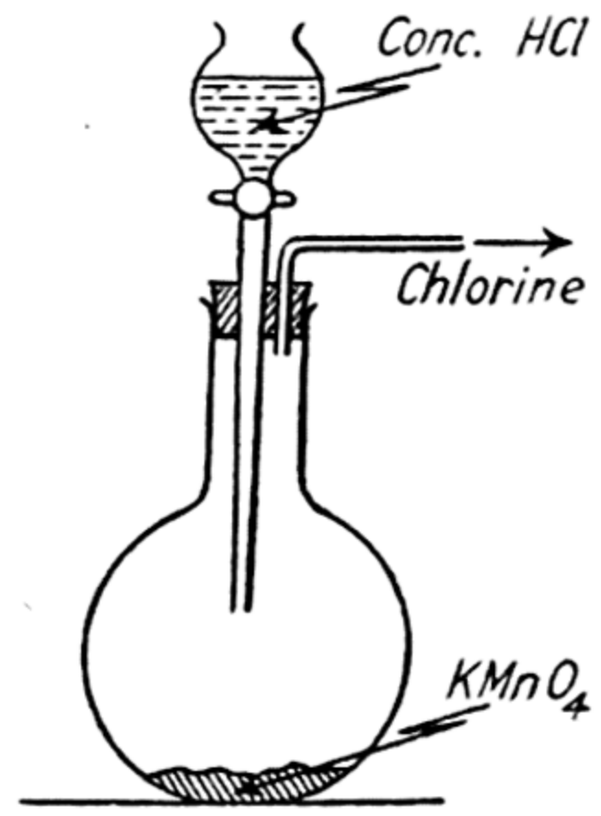


FIG. 241. Preparation of Chlorine

be purified by bubbling through water to remove hydrogen chloride and then through concentrated sulphuric acid to dry it. In the case of bromine, the reaction is usually carried out in a retort and the bromine distilled over; whilst in the case of iodine, the latter is separated by condensing the iodine vapours on a cool surface, as illustrated in the diagram (Fig. 240).

A modification of the above method is to treat the manganese dioxide directly with concentrated hydrochloric acid and heat, but if potassium permanganate be used instead of the manganese dioxide, the reaction occurs readily at ordinary temperatures, a suitable form of apparatus being as shown—

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2\uparrow + 8H_2O$$

Since HBr and HI are both more easily oxidized (HI>HBr) than HCl,

less powerful oxidizing agents may be used in these cases. Thus solutions of ferric salts, hydrogen peroxide, chlorine, etc., all liberate iodine from solutions of HI at ordinary temperatures, and even the oxygen of the air slowly liberates free iodine—

$$2FeCl_3 + 2HI = 2FeCl_2 + 2HCl + I_2$$
$$H_2O_2 + 2HI = 2H_2O + I_2$$
$$Cl_2 + 2HI = 2HCl + I_2$$

Chlorine is also produced at ordinary temperatures by the action of dilute acids on hypochlorites and bleaching powder—

$$NaOCl + 2HCl = NaCl + H_2O + Cl_2\uparrow$$

an intermediate reaction in such cases being the formation of hypochlorous acid, which is stable only in dilute solutions—

$$NaOCl + HCl = NaCl + HOCl$$
$$HOCl + HCl = H_2O + Cl_2$$

Hypobromites are unimportant and the existence of hypo-iodites is doubtful.

Very pure chlorine may be prepared by the electrolysis of fused silver chloride using carbon electrodes.

Chlorine (or chlorine-water) will displace bromine and iodine from solutions of their simple salts; bromine similarly will displace iodine from iodides—

$$Cl_2 + 2KBr = 2KCl + Br_2$$
$$Cl_2 + 2KI = 2KCl + I_2$$
$$Br_2 + 2KI = 2KBr + I_2$$

Commercial Methods of Preparation. The most important present-day source of chlorine is the by-product chlorine obtained from the electrolysis of brine in the manufacture of caustic soda (*see* p. 428). The hot chlorine evolved at the carbon anodes is first cooled to condense most of the water-vapour and then dried via concentrated sulphuric acid. After drying (but *not* before), the chlorine may be stored in iron or steel vessels. The dry chlorine is usually liquefied and supplied in small steel cylinders, usually painted yellow.

The older processes include—

(*a*) *Weldon Process.* This process represented an improvement on the original Scheele process involving the action of hot concentrated hydrochloric acid on pyrolusite (impure MnO_2)—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2\uparrow + 2H_2O$$

The spent liquors (mainly $MnCl_2$) were neutralized with limestone (to remove the residual HCl) and then treated with excess of milk of lime—

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 \downarrow + CaCl_2$$

The suspension of manganese hydroxide was then heated to about 60°C by passing in steam and then oxidized to manganic hydroxide by blowing air through it. The latter, being amphoteric, combines with the excess of milk of lime to form calcium manganite—

$$2Mn(OH)_2 + 2Ca(OH)_2 + O_2 = 2CaMnO_3 + 4H_2O$$

The resulting "Weldon mud" of $CaMnO_3$ is then used to regenerate more chlorine by the action of fresh HCl. (Note the ease with which manganous hydroxide is oxidized in alkaline solution, and that $CaMnO_3$ behaves virtually as MnO_2.)

(*b*) *Deacon's Process.* In this process HCl gas mixed with about four times its volume of air is preheated to about 450°C and passed over porous earthenware impregnated with copper chloride contained in vertical cylinders. The net reaction is—

$$4HCl + O_2 = 2Cl_2 + 2H_2O + 28{,}000 \text{ cal.}$$

The catalytic action of the copper chloride is considered to result from the decomposition of cupric chloride, followed by regeneration of more cupric chloride, and so on—

$$2CuCl_2 = Cu_2Cl_2 + Cl_2 \uparrow$$

$$2Cu_2Cl_2 + O_2 + 4HCl = 4CuCl_2 + 2H_2O$$

The disadvantages of the process are briefly that the resulting chlorine is too dilute for it to be liquefied, and the catalyst needs frequent renewal. After removal of the HCl and steam by washing, the dilute chlorine is used directly in the manufacture of bleaching powder (*see* p. 804).

The two most important processes for obtaining bromine are—

From the Stassfurt Deposits. The mother liquor remaining after crystallizing out most of the potassium and magnesium chlorides contains about 0·25 per cent of bromine as magnesium bromide. By passing chlorine counter-current up a tower down which flows the mother liquor the following reaction occurs and the liberated bromine is carried over as a vapour—

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2$$

This is condensed in earthenware coils immersed in water. Uncondensed bromine and the excess chlorine are absorbed by wet iron filings (forming $FeCl_3$ and $FeBr_2$) and the $FeBr_2$ subsequently used to produce more bromine.

From Sea Water. The very small quantities of bromine (as bromide) contained in sea water (65–70 parts per million) are now recovered commercially by the following sequence of reactions—

(i) Treatment with chlorine liberates the bromine which forms a very dilute solution in the water—

$$Cl_2 + 2NaBr = 2NaCl + Br_2 \uparrow$$

(ii) By blowing air through this dilute solution, the bromine is driven off as the vapour, but this has to be concentrated before it can be separated.

(iii) This concentration is effected by mixing the moist bromine-containing air with sulphur dioxide and passing through an absorption tower—

$$Br_2 + SO_2 + 2H_2O = 2HBr + H_2SO_4$$

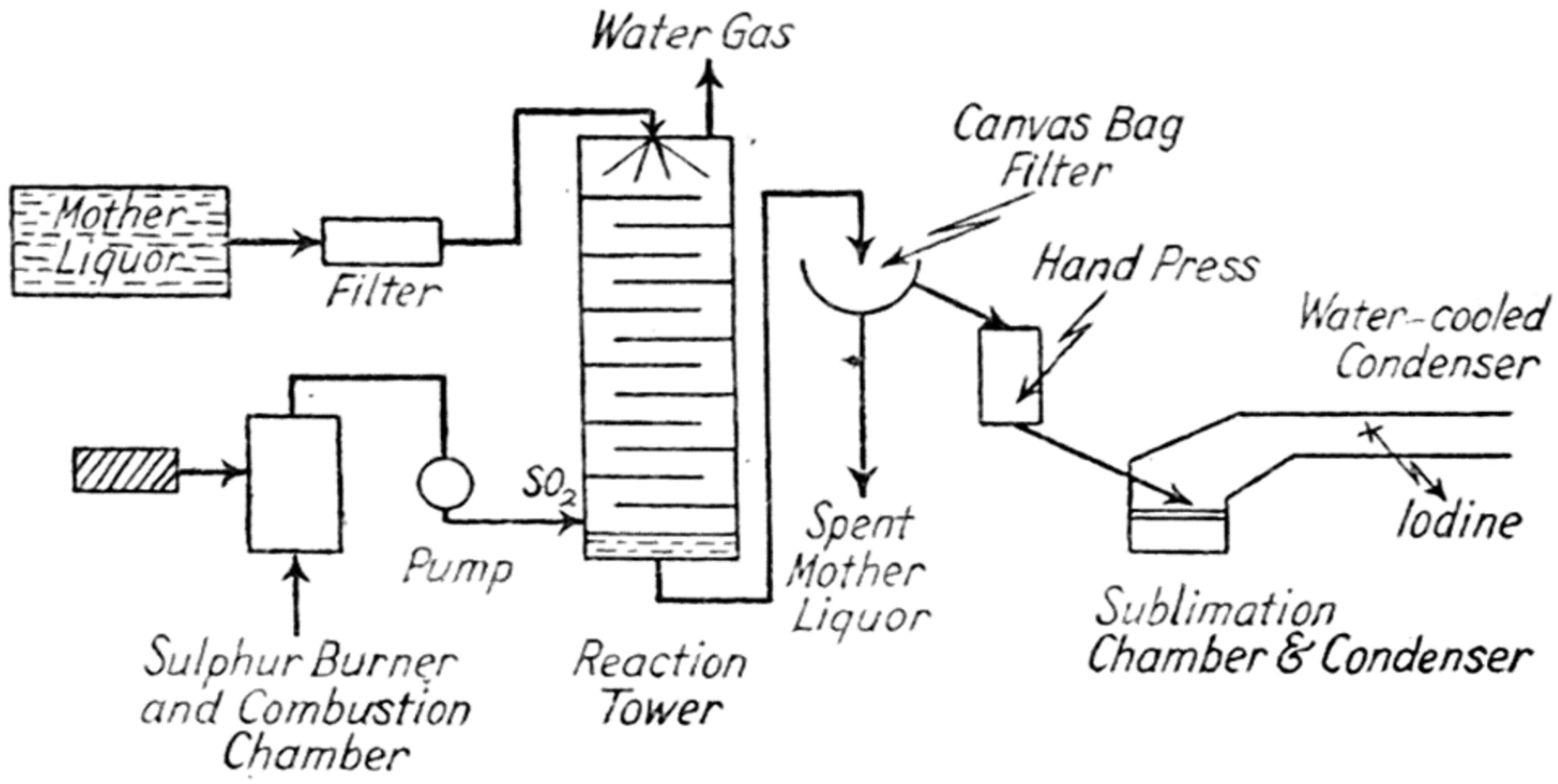


FIG. 242. Iodine from Chilean Nitrate Mother Liquor

The solution of HBr (and Br_2) so produced is continuously recirculated in the tower against fresh bromine-containing air until its concentration is sufficient for the final stage.

(iv) Treatment with chlorine then liberates bromine in sufficient concentrations for it to be distilled over and condensed.

Commercial bromine may be freed from chlorine impurity by distilling it with a metallic bromide, and may be dried by anhydrous calcium bromide—

$$FeBr_2 + Cl_2 = FeCl_2 + Br_2 \uparrow$$

The three most important processes for iodine are—

From Chile Saltpetre Deposits. The mother-liquor obtained from the purification of the crude Chile saltpetre ($NaNO_3$) contains about 6–12 g of iodine (mainly as $NaIO_3$) per litre. The liquor is passed down a tower up which passes a stream of sulphur dioxide gas—

$$2NaIO_3 + 4H_2O + 5SO_2 = Na_2SO_4 + 4H_2SO_4 + I_2$$

The iodine is filtered off through canvas bags, which are then squeezed

to remove the bulk of the moisture. The resulting cake (containing about 80 per cent of iodine) is then sublimed from cement-lined retorts and the iodine vapour condensed in earthenware pipes.

From Oil-well Brines. These contain from 30–70 parts of iodide per million. Various processes have been described, but the two most important appear to be—

(i) A process similar to that involved in the recovery of bromine from sea water described above. The stages are the same, (*a*) liberation of the iodine, (*b*) removal of the iodine as vapour, (*c*) conversion into HI and concentration by means of sulphur dioxide, and (*d*) treatment with chlorine to reliberate the iodine which is filtered off.

(ii) Silver iodide process; treatment of the brine with a 2 per cent solution of silver nitrate, containing a little ferric chloride as a coagulant, produces a mixed precipitate of silver iodide and ferric hydroxide. After treatment of this precipitate with concentrated HCl to dissolve the $Fe(OH)_3$, steel scrap is added to give a solution of ferric iodide—

$$2AgI + Fe = FeI_2 + 2Ag$$

The action of oxidizing agents, such as nitric acid or chlorine, then liberates the iodine which is filtered off and purified by melting under concentrated sulphuric acid.

From Sea-weed. The sea-weed, after drying, is carefully burnt and the ash then extracted with water. After crystallizing out most of the potassium sulphate, potassium and sodium chlorides, the mother liquor containing bromine as sodium bromide is *either* heated with manganese dioxide and concentrated sulphuric acid *or* treated with chlorine to liberate the iodine. In the former case, the iodine distils over and is condensed; in the latter, the iodine is precipitated.

Commercial iodine may be purified from bromine and chlorine by mixing it with potassium iodide and subliming off the iodine.

Properties of Chlorine, Bromine and Iodine. The solubility in water decreases from chlorine to iodine.

Chlorine. One volume of water dissolves 4·6 volumes chlorine at 0°C. If the resulting solution, known as *chlorine-water*, be cooled to 0°C, yellow octahedral crystals of chlorine-hydrate of composition $Cl_2 . 8H_2O$ separate.

Some of the dissolved chlorine reacts with the water to form hypochlorous and hydrochloric acids—

$$H_2O + Cl_2 = HCl + HOCl$$

and if the solution is exposed to bright sunlight, oxygen is liberated by the decomposition of the hypochlorous acid—

$$2HClO = 2HCl + O_2 \uparrow$$

The bleaching action of moist chlorine is attributed to the oxidizing

action of the hypochlorous acid, since dry chlorine does not bleach. It should be noted that the bleaching action is limited to organic dyestuffs, such as plant pigments, aniline dyes, etc., that is, compounds which can easily be oxidized to colourless *leuco* compounds; mineral pigments, such as printer's ink based on carbon, are not bleached.

Bromine. 100 g of water dissolve 4·3 g of bromine at 0°C. The resulting solution, known as *bromine-water*, finds many uses as a laboratory reagent, particularly in organic chemistry where it is often used as a test for unsaturation (*see* p. 872). The bromine does not react with the water to form a hypobromous acid (HOBr). It does, however, show oxidizing power in presence of easily oxidizable compounds and is a milder bleaching agent than chlorine.

Iodine. 100 g of water dissolves about 0·03 g of iodine at 25°C. It is however much more soluble in solutions of potassium iodide, the resulting solution containing the unstable potassium tri-iodide—

$$KI + I_2 = KI_3$$

The halogens are also soluble in organic solvents, the resulting colour often being used to identify the particular halogen,

Halogen	*Solvent*	*Colour*
Chlorine	Carbon tetrachloride	Colourless
Bromine	Chloroform, benzene, carbon disulphide, etc.	Orange-red
Iodine	Chloroform, benzene, carbon disulphide, etc.	Violet
	Alcohol, ether, acetone	Brown

Action on Non-metals. General reactivity decreases from fluorine to iodine.

Hydrogen. All the halogens combine directly with hydrogen, but the affinity decreases rapidly from fluorine to iodine. It has already been remarked that *fluorine* will explode with hydrogen even at −253°C. With *chlorine* the reaction occurs slowly at ordinary temperatures on exposure to diffused daylight, but occurs explosively in direct sunlight. *Bromine* vapour will not explode in hydrogen but reaction occurs on heating, and still higher temperatures are required in the case of *iodine*. In all these cases the corresponding hydrogen halide (HCl, HBr and HI) is formed.

The explosive nature of the reaction of chlorine and hydrogen in the presence of direct sunlight is due to photochemical activation followed by a "chain reaction." The absorption of a quantum of light energy, $h\nu$, results in the dissociation of a molecule of chlorine into the very reactive chlorine atoms

$$Cl_2 + h\nu = Cl + Cl$$

The following "chain-reaction" then occurs extremely rapidly to produce the phenomenon of a gaseous explosion—

$$H_2 + Cl = HCl + H$$
$$Cl_2 + H = HCl + Cl$$

The dissociation of one molecule of chlorine into free atoms can thus bring about the combination of a very large number of molecules of chlorine and hydrogen, since, as the above equations show, the reactive chlorine atom is repeatedly reliberated. Gaseous explosions mostly take place as a result of such chain reactions, although the initial disruption of one of the reacting molecules into reactive free atoms or free radicals may be brought about not only by the action of light (i.e. photo-chemical) but also by the absorption of heat (i.e. thermal) or of electrical energy.

The affinity of chlorine for hydrogen is also revealed by such reactions as—

(*a*) The burning of hydrogen at a jet in an atmosphere of chlorine, a reaction which is the essence of the commercial method for preparing hydrochloric acid.

(*b*) The burning of hydrocarbons in chlorine, e.g. candle, wax taper, turpentine (which may ignite spontaneously). In all these cases, the hydrocarbon burns with a very smoky flame due to the liberation of carbon—

$$C_nH_m + \tfrac{1}{2}mCl_2 = nC + mHCl$$

Other non-metals. The compounds formed by the halogens with the non-metals are all covalent. They are therefore gases or volatile liquids or solids and are easily hydrolyzed by water. The only such compounds that are not hydrolyzed by water appear to be SF_6 (all other sulphur-halogen compounds hydrolyzed); PF_5 (all other phosphorus halides hydrolyzed); NF_3 (all other nitrogen halides hydrolyzed); and the halogen compounds of carbon, such as CCl_4, CF_4, etc.

Chlorine combines *directly* with all the non-metals, with the exception of carbon, nitrogen and oxygen (although the chlorine compounds of these elements may be prepared indirectly). The non-reactivity of chlorine with carbon accounts for the use of this latter element as the electrode in electrolytic processes involving the liberation of chlorine—for example, the use of carbon anodes in the electrolysis of aqueous NaCl solutions.

Sulphur. Reaction with chlorine occurs on heating to give sulphur monochloride, S_2Cl_2, a yellow liquid, b. p. 140°C. SCl_2 and SCl_4 are also known. Sulphur monobromide, S_2Br_2, is prepared by dissolving sulphur in bromine, or by heating bromine with sulphur. No sulphur compounds of iodine are known.

Phosphorus. Reaction occurs with each of the halogens on heating to give compounds such as PCl_3 (phosphorous chloride) and PCl_5 (phosphoric chloride), the resulting compound depending upon the relative

proportions of phosphorus and halogen taking part in the reaction. PI_3 and P_2I_4 are known, but not PI_5.

Action on Metals. The halogens will combine directly with practically all metals under the right conditions. Thus, the alkali and alkaline-earth metals, magnesium, zinc, tin, copper and antimony all burn brightly when heated in chlorine. In general the highest chloride is formed, unless this happens to be unstable at the temperature of the reaction. Thus tin gives stannic chloride and not stannous chloride, iron forms ferric chloride, and so on. Some finely divided-metals ignite spontaneously in chlorine at ordinary temperatures, e.g. powdered antimony sprinkled into a jar of chlorine produces a shower of sparks.

The reactions with bromine and iodine are similar, but higher temperatures are required. The reaction of iodine with mercury is interesting since it occurs at ordinary temperatures. If mercury is rubbed with excess of iodine, red mercuric iodide, HgI_2, is formed, but if the mercury is in excess, the product is the green mercurous iodide, Hg_2I_2.

The use of iron filings to trap any uncondensed bromine vapour in the commercial manufacture of bromine has already been described.

The colour of certain metallic iodides is often used as a confirmatory test for the metal in qualitative analysis. The best known in this connexion are lead iodide, which crystallizes out on cooling the colourless hot solution as golden-yellow spangles; silver iodide, a yellow, curdy precipitate formed on adding silver nitrate solution to a soluble iodide; mercurous iodide, green; and mercuric iodide, scarlet.

Other Reactions. Carbon monoxide combines with chlorine on exposure to bright sunlight or in presence of a charcoal catalyst to form carbonyl chloride, also known as phosgene, $COCl_2$—

$$CO + Cl_2 = COCl_2$$

Ammonia reacts with chlorine to form hydrochloric acid and either nitrogen or the explosive nitrogen tri-chloride, depending upon whether the ammonia or the chlorine is in excess—

$$2NH_3 + 3Cl_2 = N_2 + 6HCl$$
$$NH_3 + 3Cl_2 = NCl_3 + 3HCl$$

Sulphur dioxide forms sulphuryl chloride with chlorine in direct sunlight, especially if a little camphor be present as a catalyst—

$$SO_2 + Cl_2 = \underset{\substack{\text{sulphuryl}\\\text{chloride}}}{SO_2Cl_2}$$

The *oxidizing* action of the halogens is revealed by such reactions as—

$$Cl_2 + H_2O + Na_2SO_3 = 2HCl + Na_2SO_4$$
$$H_2S + \underset{\text{water}}{Br_2} = 2HBr + S$$

and by the displacement reactions of the halogens, which also reveals a decrease in oxidizing power from chlorine to iodine—

$$2KBr + Cl_2 = 2KCl + Br_2$$
$$2KI + Cl_2 = 2KCl + I_2$$
$$2KI + Br_2 = 2KBr + I_2$$

That iodine is an oxidizing agent, although a less powerful one than chlorine (and bromine), is shown by its ability to oxidize sulphuretted

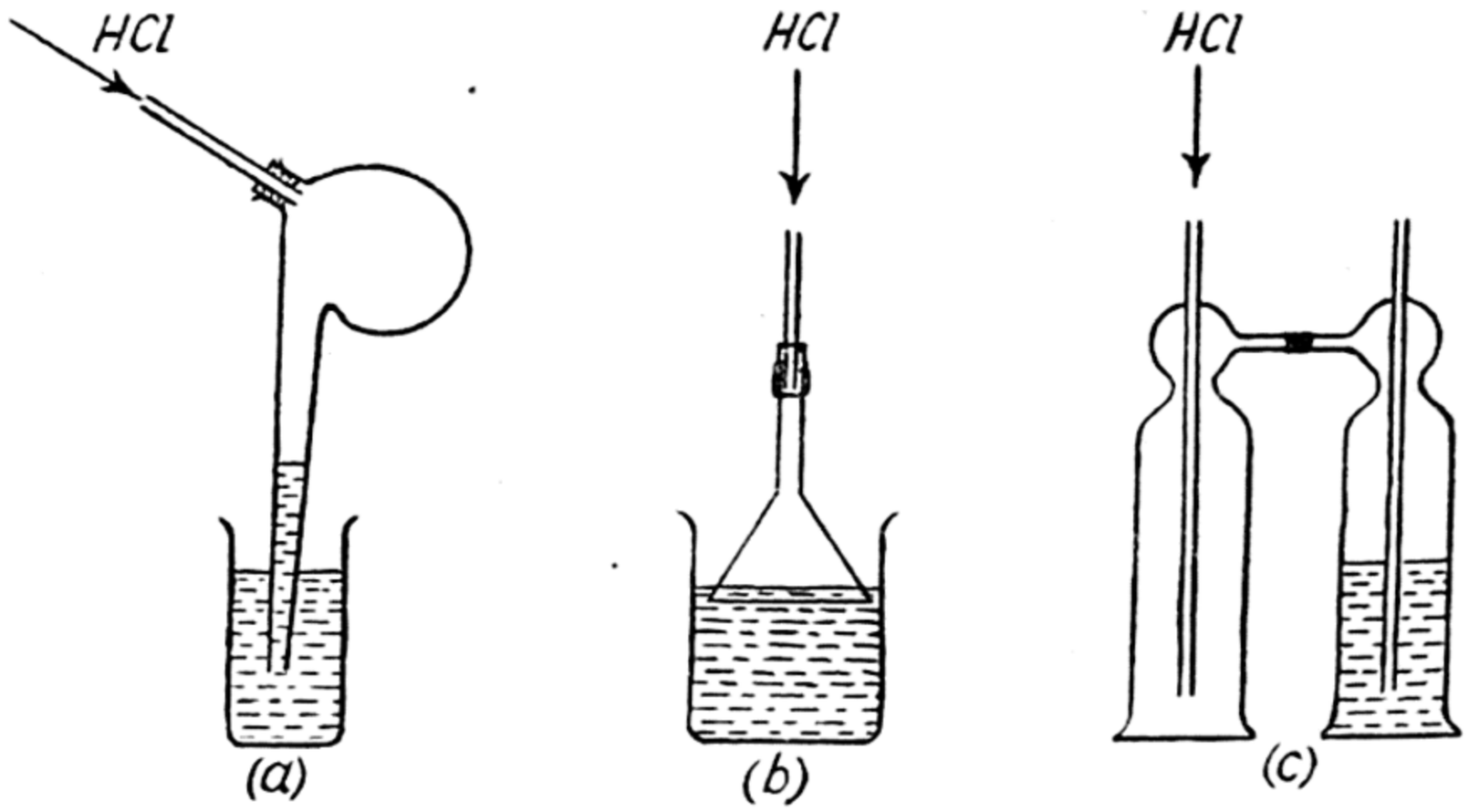


FIG. 243. Three Methods for Preventing "Sucking-back"

hydrogen to sulphur, sulphites to sulphates, arsenites to arsenates, and thiosulphate to tetrathionate—

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

In the latter case, more complete oxidation occurs with bromine and with chlorine, to give mainly sodium bisulphate, $NaHSO_4$.

HALOGEN ACIDS

The hydrogen compounds of the halogens (HCl, HBr and HI) are all gases having the covalent structures, H—Cl, H—Br and H—I. In this state they are not acids, and are referred to as hydrogen chloride, hydrogen bromide and hydrogen iodide.

They are all very soluble in water to produce strong acids. In this state, they have the ionic structure, for example, H^+Cl^-, and the solutions are known as hydrochloric acid, etc.

Hydrochloric Acid. Hydrogen chloride may be prepared by the action of hot concentrated sulphuric acid on a chloride, such as sodium chloride—

$$NaCl + H_2SO_4 = HCl\uparrow + NaHSO_4$$

The reaction $$NaHSO_4 + NaCl = Na_2SO_4 + HCl\uparrow$$

only occurs above about 500°C. Since the gas (HCl) is extremely soluble in water, it is collected by the upward displacement of air. If the solution is required the usual precautions must be taken to prevent sucking-back, as shown in Fig. 243.

Commercial Preparation. Hydrochloric acid is prepared by the combustion of hydrogen in chlorine, followed by solution in water. The acid so produced is much purer than that produced by the older method involving the action of concentrated sulphuric acid on salt. Traces of chlorine in the final acid may be removed by treatment with scrap copper (which combines with any chlorine present to form cupric chloride), followed by distillation.

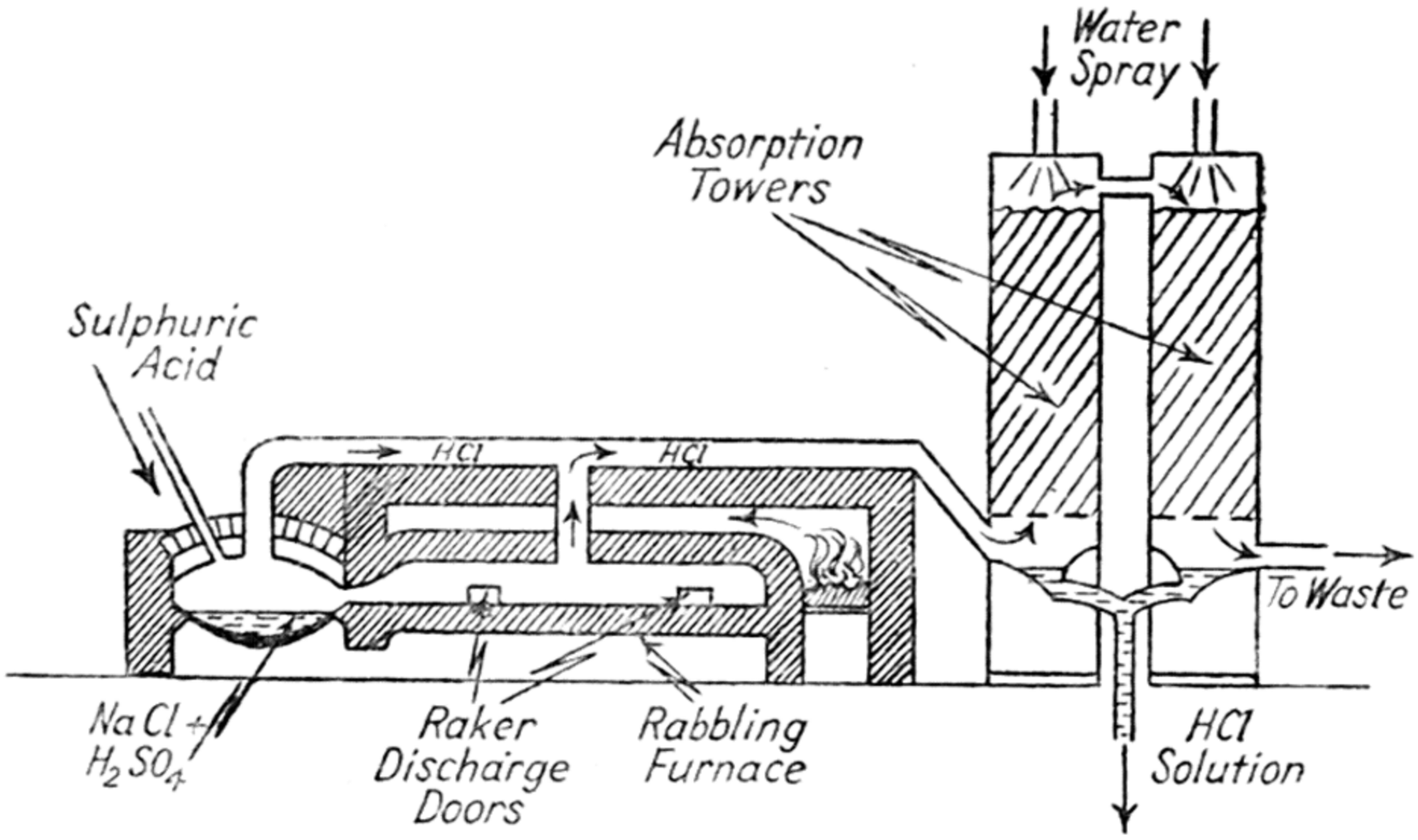


FIG. 244. Salt-cake Furnace

For a long time, the only source of hydrochloric acid was that produced as a by-product in the first stage of the Leblanc process for sodium carbonate. Although sodium carbonate is not nowadays manufactured by this process, considerable quantities of sodium sulphate are still produced by the action of concentrated sulphuric acid on common salt. The reaction is carried out in two stages, corresponding with the two equations given opposite. The first stage is carried out in a shallow cast-iron pan of the furnace shown in the diagram. The fused mass is then raked into a second portion of the furnace where it is heated to redness to form sodium sulphate and liberate more hydrogen chloride. The latter is passed through a series of coke-filled absorption towers down which passes a spray of water to form a solution of hydrochloric acid, or *spirits of salt*.

Hydrobromic and Hydriodic Acids, HBr and HI. In addition to their acidic properties, these two compounds are also reducing agents, and this property considerably modifies their chemical behaviour when compared with hydrochloric acid. This development of reducing properties in the

hydrogen compounds of the halogens runs parallel to the decrease in oxidizing power of the halogens themselves—

Cl_2, Br_2, I_2 → decreasing oxidizing power

HCl, HBr, HI → increasing reducing power

The first result of the reducing properties of HBr and HI to be noted is that these two acids may not be prepared by the concentrated sulphuric acid method described for HCl. The HBr (or HI) first liberated, reacts with the sulphuric acid, which is itself also an oxidizing agent when hot and concentrated—

$$KBr + H_2SO_4 = HBr\uparrow + KHSO_4$$

$$2HBr + H_2SO_4 = Br_2\uparrow + SO_2\uparrow + 2H_2O$$

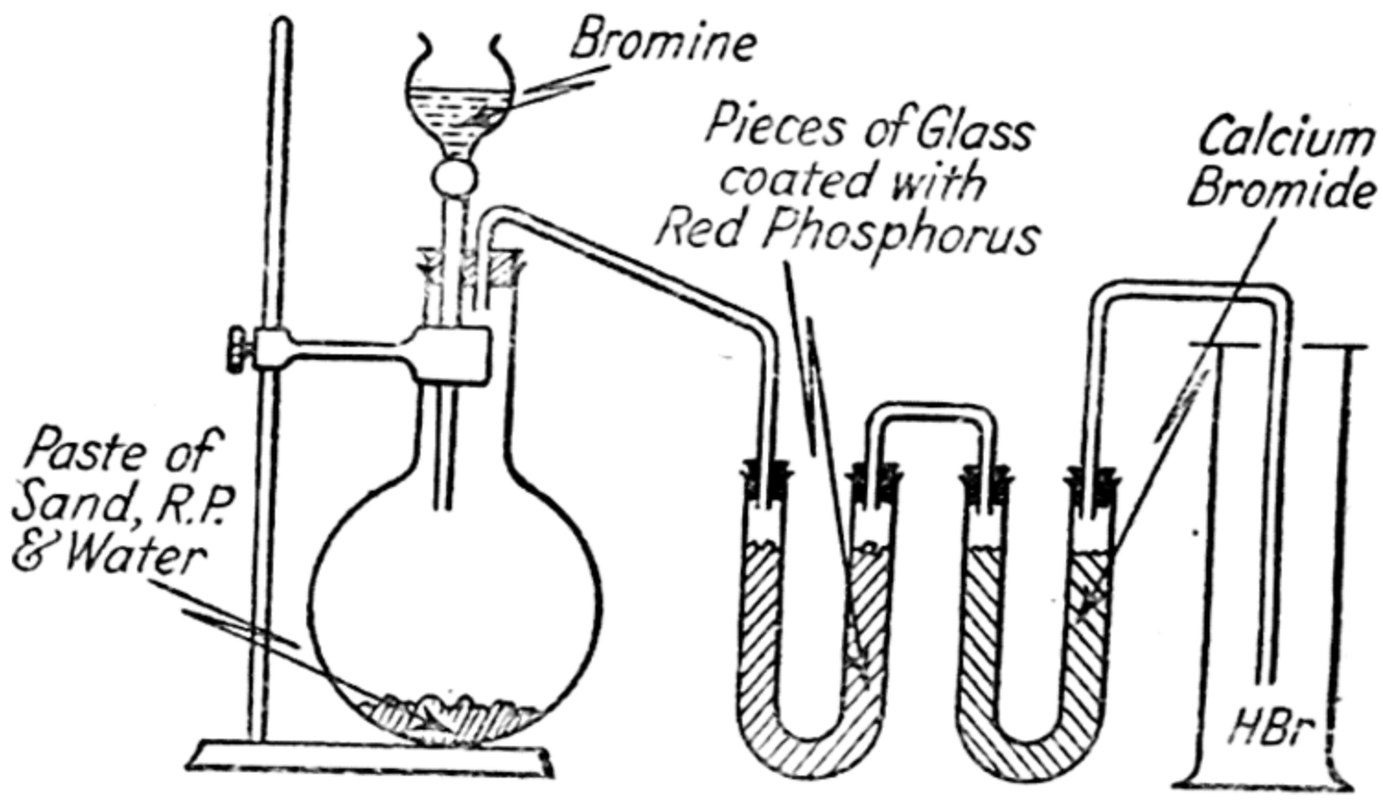


FIG. 245. Preparation of Hydrogen Bromide

so that when a bromide is heated with concentrated sulphuric acid, not only is the colourless fuming HBr gas evolved, but also the heavy red fumes of bromine vapour. Similar reactions occur in the case of the iodide, but here the stronger reducing action of the HI shows itself in the further reduction of the sulphuric acid to sulphuretted hydrogen—

$$KI + H_2SO_4 = HI\uparrow + KHSO_4$$

$$2HI + H_2SO_4 = I_2\uparrow + SO_2\uparrow + 2H_2O$$

$$8HI + H_2SO_4 = 4I_2\uparrow + H_2S\uparrow + 4H_2O$$

In this case, when an iodide is heated with concentrated sulphuric acid, violet fumes of iodide vapour are evolved together with the colourless fuming HI gas. These reactions should be particularly noted in connexion with the procedure for detecting negative radicals in qualitative analysis which involves the action of concentrated sulphuric acid on the unknown solid.

HBr and HI may however be prepared by the action of an acid on the corresponding salt, if the acid chosen has a relatively high boiling point

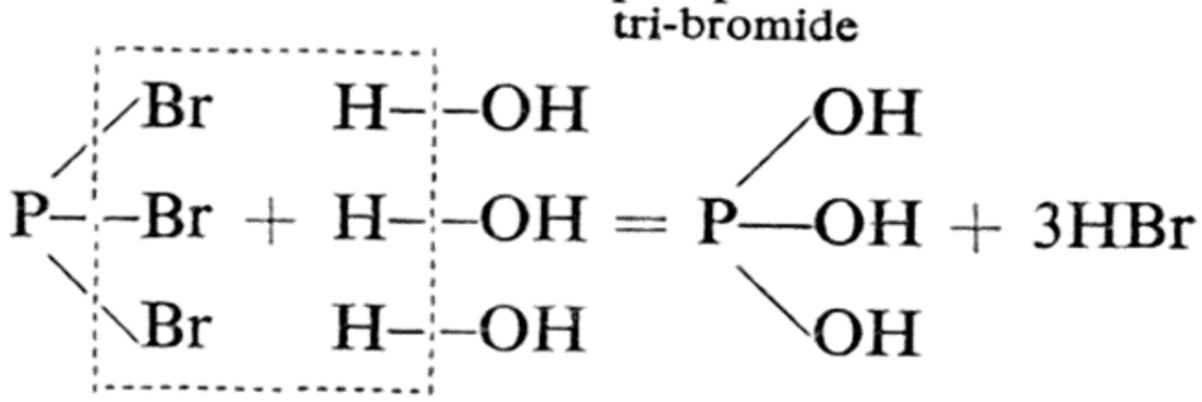
(like sulphuric acid), but is *not* an oxidizing agent. Phosphoric acid, H_3PO_4, may be used, but the rate of the reaction is very slow with the bromide. With iodides, relatively pure HI may be liberated on heating—

$$KI + H_3PO_4 = KH_2PO_4 + HI \uparrow$$

The *usual laboratory method* of preparing these acids is by hydrolysis of the corresponding phosphorus halides, PBr_3 and PI_3. The reaction is carried out, in the case of HBr, by running liquid bromine slowly into a paste of red phosphorus and water, contained in a round-bottomed flask as shown in Fig. 245.

$$2P + 3Br_2 = 2PBr_3$$

phosphorus tri-bromide

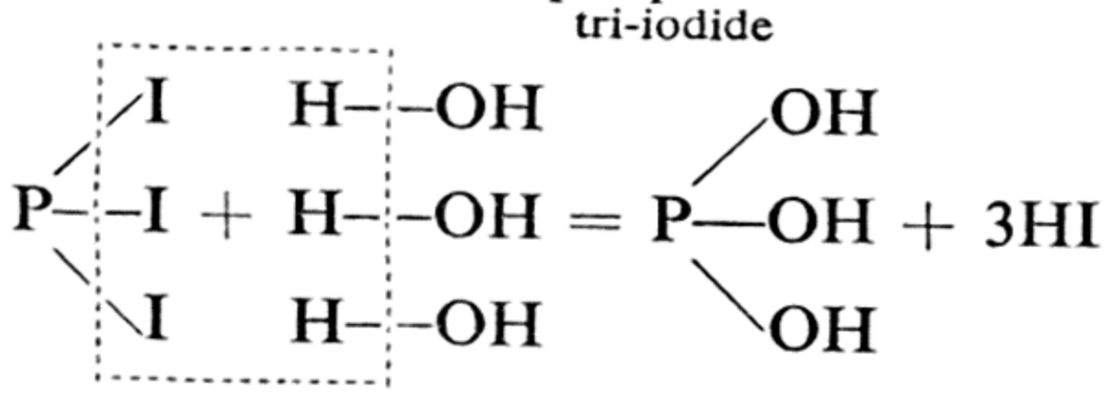


Any bromine vapour carried over with the hydrogen bromide is trapped by the red phosphorus contained in the U-tube, the HBr passing on. After drying by passing through a second U-tube of calcium bromide, the gas is collected by the upward displacement of air. If a solution of hydrobromic acid is required, the same precautions to prevent sucking-back must be adopted as were observed in the case of hydrochloric acid.

In the case of hydrogen iodide, it is necessary to place the iodine in the flask at the beginning of the preparation. In this case, the water is placed in the dropping funnel and dry red phosphorus mixed with the iodine in the flask. The following reactions occur on admitting the water gradually from the tap-funnel.

$$2P + 3I_2 = 2PI_3$$

phosphorus tri-iodide



The apparatus is the same as that for hydrogen bromide, except that the drying-tube in this case contains calcium iodide instead of calcium bromide. The same precautions are observed if a solution of hydriodic acid is required as were observed for HCl and HBr. The compound $P(OH)_3$, which remains in the flask, is known as phosphorous acid, and is more usually depicted as H_3PO_3.

Larger quantities of hydrobromic acid may be prepared by the action of bromine on benzene in presence of dry aluminium powder as catalyst. The reaction is carried out in apparatus similar to that described above for HBr and HI, except that an additional U-tube containing anthracene to absorb benzene vapour is introduced after the U-tube containing the red phosphorus. The reaction is initiated by gently heating the flask, and then slowly adding the bromine.

$$C_6H_6 + Br_2 = C_6H_5Br + HBr$$

A solution of hydriodic acid may be prepared by passing sulphuretted hydrogen into a suspension of iodine in water—

$$H_2S + I_2 = 2HI + S\downarrow$$

Properties of HCl, HBr and HI. They are all colourless gases at ordinary temperatures, and are extremely soluble in water to form strong acids. For this reason they fume in moist air due to the formation of droplets of hydrochloric acid, etc. With ammonia, white fumes of the corresponding ammonium halides are formed, e.g.

$$NH_3 + HI = NH_4I$$

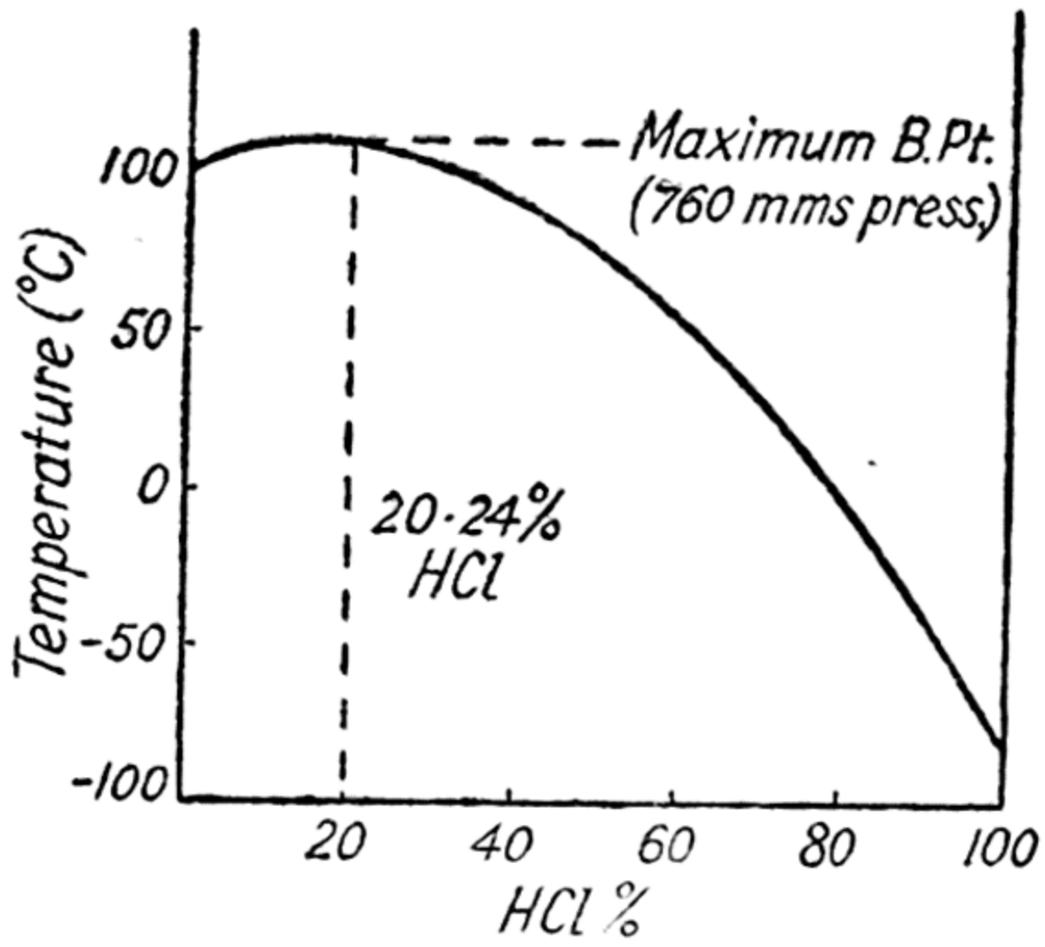


FIG. 246. Boiling-points of Hydrochloric Acid Solutions at 760 mm Pressure

The very soluble nature of these hydrogen halides is often demonstrated in the laboratory by the "fountain" experiment (*see* p. 638).

Commercial concentrated hydrochloric acid contains about 28 per cent of HCl by weight, and boils at 108°C. If this solution is boiled, the boiling point slowly increases due to a higher rate of loss of HCl until the boiling point reaches a maximum at 110°C at 760 mm pressure. The solution then boils unchanged at this temperature, that is no further decrease in concentration occurs no matter how long the solution be boiled, both the solution and the distillate containing 20·24 per cent HCl. Such a solution is known as a *constant boiling-point mixture*. The same solution would ultimately be obtained if a weaker solution of HCl were boiled, as indicated by the boiling-point concentration diagram (Fig. 246). It should be noted that this property of forming a constant boiling mixture may be utilized in the laboratory to prepare a standard solution of the acid. A given hydrochloric acid solution is allowed to boil until its boiling point increases to 110°C at 760 mm pressure, when it must contain 20·24 per cent HCl. Since

both the composition and boiling point are slightly affected by variations in the atmospheric pressure, it is clear that the maximum boiling mixture is not a true compound. The other halogen acids also form mixtures of maximum boiling point with water, as indicated in the following table.

TABLE 107

Composition and Boiling Points of Halogen Acids of Maximum Boiling Points

Acid	Percentage Acid by Weight	Boiling Point (760 mm)
Hydrofluoric acid .	37·00	120°C
Hydrochloric acid .	20·24	110°C
Hydrobromic acid .	48·00	126°C
Hydriodic acid .	58·00	127°C

Chemical Properties of the Halogen Acids. Apart from the usual properties associated with a strong acid, such as reaction with metals to liberate hydrogen, reaction with bases to form salts, etc., the chemistry of these acids is complicated by the reducing properties shown by HI and to a lesser degree by HBr; HCl appears to be a much weaker reducing agent. This development of reducing properties is primarily due to a decrease in electronegative character of the parent halogen, from fluorine to iodine, so that the compound with hydrogen becomes less and less stable. The heats of formation of the gases from their elements are a measure of this increasing instability—

Gas	Heat of Formation	Stability
Hydrogen fluoride .	+ 147,000 cals	↓ decreasing
Hydrogen chloride .	+ 22,000 cals	
Hydrogen bromide .	+ 8,600 cals	
Hydrogen iodide .	+ 3,000 cals	

It follows from these results that hydrogen iodide should tend to dissociate into hydrogen and iodine. The reaction—

$$H_2 + I_2 \rightleftharpoons 2HI$$

is in fact reversible, the equilibrium concentration of HI decreasing with increase in temperature, as shown in the following table.

Temperature	Percentage Dissociation of HI	Equilibrium Concentration of HI (percentage)
283°C	17·9	82·1
444°C	22·0	78·0
527°C	24·7	75·3

The reaction was studied by Bodenstein. Hydrogen and iodine were heated together in various proportions in sealed tubes at constant elevated temperatures (e.g. 450°C). After a time, sufficiently long for equilibrium to be established, the tubes were suddenly cooled to prevent further reaction. The tubes were then broken open and the composition of the mixture determined by simple analysis.

$$\text{The equilibrium constant,} \quad K = \frac{[HI]^2}{[H_2]\,[I_2]}$$

Starting with a g.mol of H_2 and b g.mol of I_2, then if $2x$ g.mol of HI are formed at equilibrium, it follows that—

$$K = \frac{(2x/V)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)\,(b-x)}$$

The *reducing properties* of solutions of hydriodic acid are shown by the liberation of iodine when it is treated with any of the common oxidizing agents, thus—

$$H_2O_2 + 2HI = 2H_2O + I_2$$
$$Cl_2 + 2HI = 2HCl + I_2$$
$$2FeCl_3 + 2HI \rightleftharpoons 2FeCl_2 + I_2 + 2HCl$$

This latter reaction is however reversible, as also are such reactions as

$$Na_3AsO_4 + 2HI \rightleftharpoons Na_3AsO_3 + H_2O + I_2$$
$$H_2SO_4 + 2HI \rightleftharpoons H_2SO_3 + H_2O + I_2$$

Since aqueous solutions of HI are slowly oxidized even by the oxygen of the atmosphere—

$$4HI + O_2 = 2H_2O + 2I_2$$

it is usual whenever HI is required as a reducing agent to liberate it in situ by the action of an acid on a stable iodide, such as KI. This explains the use of potassium iodide in such volumetric estimations as the standardization of permanganate and dichromate solutions with sodium thiosulphate solutions. 25-ml portions of the permanganate (or dichromate)

solution are acidified and treated with excess of potassium iodide. An equivalent amount of iodine is liberated (the reaction occurs relatively slowly, so that it is usual to allow several minutes for completion) and this is then estimated by titration with the sodium thiosulphate.

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5\overline{O}$$
$$2HI + \overline{O} = H_2O + I_2$$
$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

If 25 ml of the permanganate solution require 20·3 ml of 0·102 N sodium thiosulphate solution, then the normality of the permanganate solution is $\frac{20{\cdot}3}{25{\cdot}0} \times 0{\cdot}102\ \text{N} = 0{\cdot}083\ \text{N}$.

Potassium iodide is also used in the volumetric estimation of copper—

$$2CuSO_4 + 4KI = (2CuI_2) + 2K_2SO_4$$
$$(2CuI_2) = Cu_2I_2 + I_2$$

25 ml of the given copper solution is treated with excess of KI, and the liberated iodine then estimated by titration with standard sodium thiosulphate, as above.

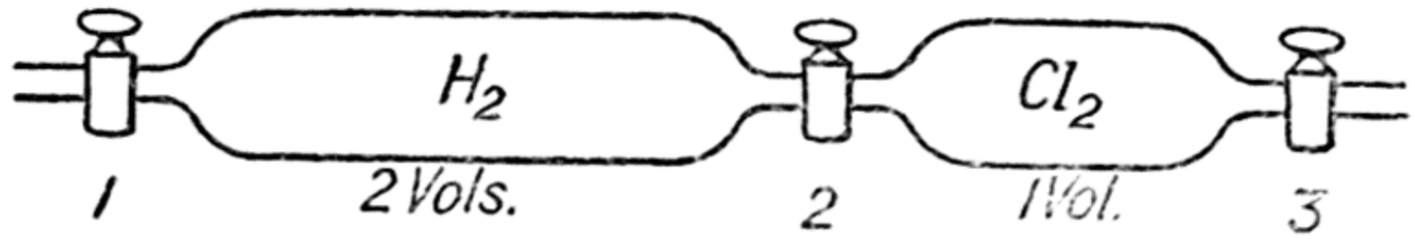


FIG. 247. Formula of Hydrogen Chloride

Formula of HCl. The formula of hydrogen chloride may be determined by the following method. The apparatus used is shown in the diagram, the larger chamber being filled with dry hydrogen and the smaller with dry chlorine. Tap 2 is opened, and the apparatus exposed to diffuse daylight for several days, during which the hydrogen and chlorine react together to form hydrogen chloride. By opening tap 1 under mercury, no mercury enters the apparatus thus showing that this reaction occurs without change in volume. Tap 1 is then closed, and then subsequently reopened under water, the apparatus being held vertically. The water rises to tap 2, that is, it completely fills the larger chamber. This shows that 2 volumes of hydrogen chloride must have been formed from the 2 volumes of H_2 and 1 volume of Cl_2. The gas remaining in the second chamber is then analyzed and shown to be hydrogen—thus one volume of hydrogen remains unchanged after the reaction. These observations may be summarized in the equation—

1 volume hydrogen + 1 volume chlorine = 2 volumes hydrogen chloride

that is 1 volume H_2 + 1 volume Cl_2 = 2 volumes H_xCl_y

whence, by Avogadro's hypothesis, since equal volumes of all gases under the same conditions of temperature and pressure must contain equal numbers of molecules—

$$H_2 + Cl_2 = 2H_xCl_y$$

Assuming the molecules of hydrogen and chlorine each to be diatomic, it then follows that the molecular formula of hydrogen chloride is HCl.

Reactions of the Halogens on the Alkalis. The reaction—

$$Cl_2 + H_2O = HCl + \underset{\text{hypochlorous acid}}{HOCl}$$

occurs to a slight extent when chlorine is dissolved in water. If a cold dilute solution of sodium hydroxide be used instead of water, the solubility of the chlorine is considerably increased, the resulting solution containing sodium chloride and sodium hypochlorite—

$$Cl_2 + 2NaOH = NaCl + NaOCl + H_2O$$

If the sodium hydroxide solution is hot, the products are sodium chloride and sodium chlorate, $NaClO_3$, the latter being formed by a self oxidation-reduction decomposition of the hypochlorite—

$$3NaOCl = 2NaCl + NaClO_3$$

and the overall reaction is expressed by the equation—

$$3Cl_2 + 6NaOH = 5NaCl + NaClO_3 + 3H_2O$$

Similar reactions occur with bromine and iodine. The resulting hypo-compounds produced in the cold are, however, less stable than the hypochlorates. The hypoiodites are in fact so very unstable that they decompose (to form the iodide and iodate) at ordinary temperatures.

OXIDES AND OXY-ACIDS OF THE HALOGENS

The following table shows the relationship between the more important oxides and the oxy-acids of chlorine.

Oxides	*Oxy-acids*
Chlorine monoxide, Cl_2O	Hypochlorous acid, $HClO$
Chlorine dioxide, ClO_2	Chlorous acid, $HClO_2$
	Chloric acid, $HClO_3$
Chlorine heptoxide, Cl_2O_7	Perchloric acid, $HClO_4$

Chlorine Monoxide, Cl_2O, is prepared by passing dry chlorine over

dry freshly precipitated mercuric oxide, and condensing the chlorine monoxide gas in a U-tube immersed in a freezing mixture—

$$2HgO + 2Cl_2 = HgO \,.\, HgCl_2 + Cl_2O$$

A basic mercuric chloride is formed at the same time.

Chlorine monoxide is a pale orange-yellow gas, which condenses at 5°C to form a reddish-brown liquid. Both the gas and the liquid are very unstable, and the decomposition may occur explosively particularly in presence of organic matter or on heating. It dissolves in water to form hypochlorous acid, and may therefore be regarded as the anhydride of this acid—

$$Cl_2O + H_2O = 2HOCl$$

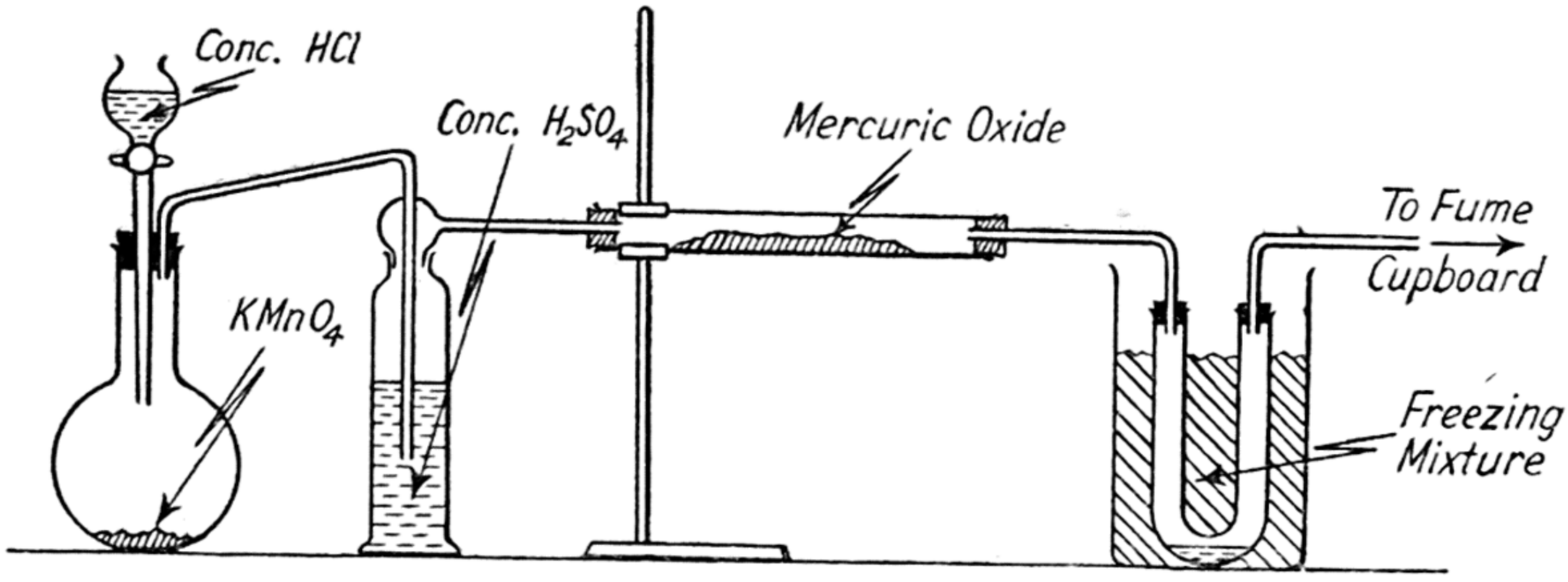


FIG. 248. Preparation of Chlorine Monoxide

Hypochlorous Acid, HOCl. The bleaching action of moist chlorine is considered due to the formation of this acid—

$$Cl_2 + H_2O = HCl + HClO$$

Small quantities of hypochlorous acid may also be prepared by dissolving chlorine monoxide in water, or by passing chlorine through a suspension of freshly precipitated yellow mercuric oxide suspended in water—

$$HgO + H_2O + 2Cl_2 = HgCl_2 + 2HOCl$$

The mercuric oxide reacts with the first-formed HCl, but not with the very weakly acidic hypochlorous acid, and the latter may be separated by distillation as a dilute solution.

Larger quantities of the acid may be obtained by the action of cold dilute acids on hypochlorites or bleaching powder, for example—

$$Ca(OCl)_2 + CO_2 + H_2O = CaCO_3 + 2HClO$$

Properties of Hypochlorous Acid. It is known only in dilute aqueous

solutions (up to about 5 per cent), and decomposes on warming or on exposure to sunlight—

$$2HClO = 2HCl + O_2\uparrow$$
$$3HClO = 2HCl + HClO_3$$

It is a weak acid, and forms salts, the hypochlorites, with the more electropositive elements (K, Na, Ca) by reaction with their hydroxides. It is a powerful oxidizing agent and bleaching agent. It liberates oxygen on exposure to sunlight, by reaction with silver oxide, and also on warming with a small amount of a cobalt salt which catalyzes the decomposition.

$$Ag_2O + 2HOCl = 2AgCl + H_2O + O_2\uparrow$$

The reaction with the cobalt salt will be referred to again in connexion with the liberation of oxygen from bleaching powder.

Hypochlorites. These are more stable than the free acid, and are much more important commercially.

Sodium Hypochlorite, NaOCl. Aqueous solutions of this salt are prepared commercially by passing chlorine into cold solutions of sodium hydroxide until the latter have been almost completely chlorinated—the residual small NaOH concentration improves the stability of the hypochlorite solution—

$$Cl_2 + 2NaOH = NaCl + NaOCl + H_2O$$

Smaller quantities are also prepared by electrolyzing cold solutions of sodium chloride in cells suitably designed so that the chlorine liberated at the anode may react with the sodium hydroxide formed at the cathode.

Like hypochlorous acid, the solution decomposes on warming—

$$3NaOCl = 2NaCl + NaClO_3$$

and is a powerful oxidizing and bleaching agent. It is used commercially mainly in the bleaching of the materials used in the artificial silk and rayon industries.

Bleaching Powder. This very important industrial material is prepared by the action of chlorine on slaked lime, $Ca(OH)_2$. The process is nowadays carried out in the Bachmann Plant as shown in the diagram opposite. The slaked-lime is conveyed by a suitable air-pumping arrangement to the top of the chlorinating tower, and fed into the tower. The slaked-lime then gradually passes down the tower against a stream of ascending chlorine gas. The rotating rakes with which each floor of the tower is equipped serve to keep the slaked-lime moving, so exposing fresh material to the action of the chlorine. The chlorination is complete by the time the slaked-lime reaches the sixth floor. The chlorine is introduced at the seventh floor, leaving the eighth and last floor for passing hot air through the bleaching powder in order to remove any uncombined free

chlorine. The bleaching powder then falls into the hopper at the base of the tower, and on opening the valve may be charged directly into barrels for distribution to industry.

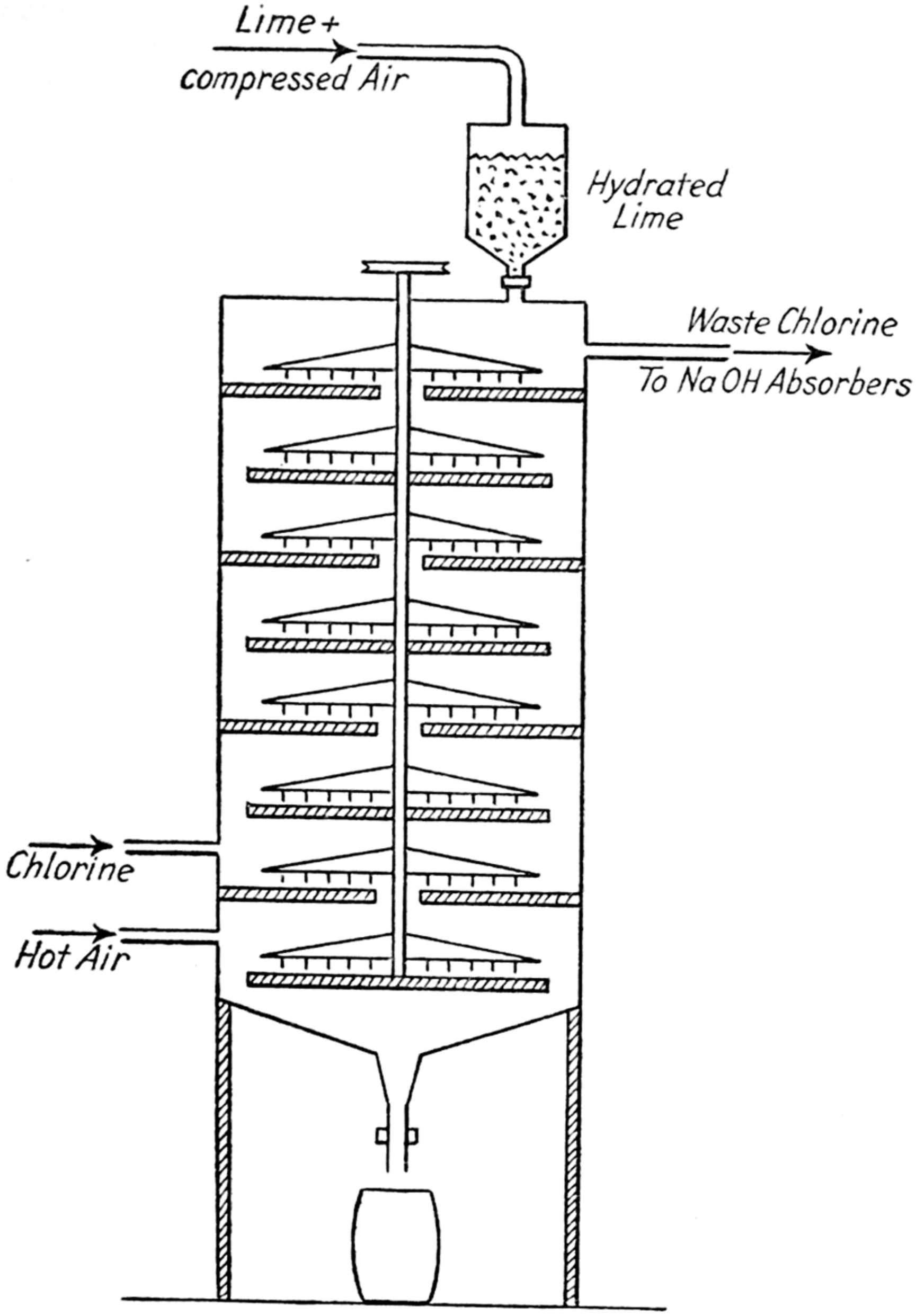


FIG. 249. Manufacture of Bleaching Powder

The formula of bleaching powder has led to much discussion. The normal reaction, by analogy with the reaction of chlorine with sodium hydroxide, might be expected to be—

$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O$$

That this equation is not entirely correct would seem to follow from the facts that—

(i) Commercial bleaching powder always contains some unchanged calcium hydroxide, which can only be further chlorinated with difficulty, and

(ii) bleaching powder is not markedly deliquescent, and this would appear to rule out the presence of free calcium chloride.

The results of X-ray studies, however, have shown that there are virtually two stages in the formation of bleaching powder. The first stage results in the formation of a basic hypochlorite, $Ca(OCl)_2 . 2Ca(OH)_2$, and a basic chloride, $CaCl_2 . Ca(OH)_2 . H_2O$. During the second stage, more of the basic chloride is formed and the basic hypochlorite is largely replaced by normal hypochlorite. Bleaching Powder may thus be regarded as an intimate mixture of $Ca(OCl)_2$ and basic calcium chloride, the latter (unlike $CaCl_2$) being not particularly deliquescent.

Properties of Bleaching Powder. Bleaching powder is the cheapest form of bleaching material available to industry, and is extensively used in the bleaching of raw cotton and wood pulp for paper making. The bleaching action is due to hypochlorous acid which is liberated when bleaching powder is treated with a dilute acid, a reaction which has already been noted in connexion with this acid—

$$Ca(OCl)_2 + CO_2 + H_2O = CaCO_3 + 2HOCl$$

Chlorine may be liberated by the decomposition of the hypochlorous acid—

$$Ca(OCl)_2 + 4HCl = CaCl_2 + 2H_2O + 2Cl_2 \uparrow$$

$$(HOCl + HCl = H_2O + Cl_2)$$

and oxygen may be liberated by warming with a dilute solution of a cobalt salt—

$$Ca(OCl)_2 = CaCl_2 + O_2 \uparrow$$

Available Chlorine. Bleaching powder is sold on its available-chlorine content, that is, the percentage of chlorine by weight which is liberated by the action of hydrochloric acid. The commercial product usually contains between 36–40 per cent of available chlorine.

$$Ca(OCl)_2 + 4HCl = CaCl_2 + 2H_2O + 2Cl_2 \uparrow$$

This reaction occurs in two stages—

(i) $$Ca(OCl)_2 + 2HCl = CaCl_2 + 2HOCl$$

(ii) $$2HOCl + 2HCl = 2H_2O + 2Cl_2 \uparrow$$

The bleaching action of bleaching powder is due to the hypochlorous acid and for this first reaction any dilute acid (sulphuric, acetic or even carbonic

acid) will be equally as effective. This fact explains the following method for determining the available chlorine in bleaching powder.

The "available chlorine" of bleaching powder is *defined* as that weight of chlorine (as the element) which has the same oxidizing power as 100 g of bleaching powder.

A weighed amount of the bleaching powder is ground up with a little water in a clean basin, and after allowing a few moments for the solid matter to settle the supernatant liquid is poured into a graduated flask. This process is repeated until the whole of the bleaching powder has been transferred to the graduated flask, and is necessitated by the presence of lime which may be coating some of the hypochlorite. After making up the volume to the graduation mark, 25-ml portions are withdrawn, acidified with acetic acid and treated with excess potassium iodide solution. The iodine liberated is then estimated by titration with standard thiosulphate solution.

$$Ca(OCl)_2 + 2HAc = CaAc_2 + 2HOCl$$
$$2HOCl + 4HI = 2HCl + 2H_2O + 2I_2$$

(*Note*: The amount of iodine liberated is equivalent to the available chlorine, as indicated by the above two equations with hydrochloric acid. The available chlorine is therefore determined by multiplying the normality of the bleaching powder solution by 35·5, the equivalent weight of chlorine, and converting this to a percentage basis.) Acetic acid is used in this titration since stronger acids would liberate chloric acid from the small quantity of calcium chlorate present in bleaching powder and this acid would then react with the hydriodic acid to liberate more iodine.

Chlorine Dioxide, ClO_2, may be prepared by gradually adding finely powdered potassium chlorate to well-cooled concentrated sulphuric acid, followed by very carefully warming, when the following reactions occur—

$$KClO_3 + H_2SO_4 = KHSO_4 + HClO_3$$
$$3HClO_3 = 2ClO_2\uparrow + HClO_4 + H_2O$$

The chlorine dioxide is evolved as a reddish-yellow gas with an unpleasant smell, and may be condensed to a dark red liquid, boiling point 9·9°C. Both the gas and liquid are very unstable, and may decompose explosively when heated or in presence of organic matter; the familiar "crackle" produced when concentrated sulphuric acid is gently warmed with a chlorate is due to this decomposition. The increasing use of chlorine dioxide in the control of pests in flour mills has led to the development of simpler methods for preparing the gas, such as displacement reactions of the type—

$$KClO_3 + NO_2 = KNO_3 + ClO_2\uparrow$$

Chlorine dioxide is a *mixed* anhydride of chlorous and chloric acids—

$$2ClO_2 + H_2O = \underset{\text{chlorous acid}}{HClO_2} + \underset{\text{chloric acid}}{HClO_3}$$

and salts of these two acids are produced when an aqueous solution of the gas is treated with sodium or potassium hydroxides.

Chlorous Acid and Chlorites. An aqueous solution of chlorous acid may be prepared by the action of very dilute sulphuric acid on a solution of barium chlorite—

$$Ba(ClO_2)_2 + H_2SO_4 = BaSO_4\downarrow + 2HClO_2$$

The colourless solution, so obtained, gradually decomposes at ordinary temperatures and chlorine and chlorine dioxide gases are evolved—

$$8HClO_2 = 6ClO_2\uparrow + Cl_2\uparrow + 4H_2O$$

The Chlorites are prepared together with chlorates by the action of chlorine dioxide on solutions of the alkalis—

$$2ClO_2 + 2NaOH = NaClO_2 + NaClO_3 + H_2O$$

but, if sodium peroxide be used, only the chlorite is formed—

$$Na_2O_2 + 2ClO_2 = 2NaClO_2 + O_2\uparrow$$

The chlorites are very powerful oxidizing and bleaching agents, and these properties account for their increasing importance (particularly sodium chlorite) in industry. They may be distinguished from hypochlorites by their bleaching action after treatment with a solution of sodium arsenite, the latter destroying the hypochlorite—

$$Na_3AsO_3 + NaOCl = Na_3AsO_4 + NaCl$$

Chloric Acid and Chlorates. A dilute aqueous solution of chloric acid, $HClO_3$, may be prepared by adding the equivalent amount of dilute sulphuric acid to an aqueous solution of barium chlorate—

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4\downarrow + 2HClO_3$$

The solution may be concentrated up to about 40 per cent concentration by allowing it to stand over concentrated H_2SO_4 in a vacuum desiccator. Stronger solutions cannot be prepared owing to the decomposition—

$$3HClO_3 = HClO_4 + 2ClO_2\uparrow + H_2O$$

The same decomposition occurs on warming the solution, and this reaction may be used to prepare chlorine dioxide.

As might be expected from its unstable nature, it is a powerful oxidizing agent. Thus hydrochloric acid is oxidized to *euchlorine*, (a mixture of chlorine and chlorine dioxide), sulphur dioxide to sulphuric acid, and hydriodic acid to iodine—

$$8HClO_3 + 16HCl = 9Cl_2\uparrow + 6ClO_2\uparrow + 12H_2O$$

Chlorates. Sodium and potassium chlorates are nowadays prepared

commercially by the electrolysis of aqueous solutions of sodium chloride or potassium chloride. If the electrolyte is heated to 45°C or higher, and the resulting sodium hydroxide moved quickly from the cathode to the anode compartment, the following reaction occurs—

$$3Cl_2 + 6NaOH = 5NaCl + NaClO_3 + 3H_2O$$

A small amount of alkali dichromate is added to the electrolyte. This addition improves the current efficiency and, by forming an insoluble film (possibly of chromium chromate) on the cathode, tends to isolate the electrolyte from the nascent hydrogen liberated there, thereby reducing the chance of chlorate (and hypochlorite) being reduced back to chloride.

Electrolysis of Brine Solutions

The following account contains a more detailed analysis of the behaviour of brine solutions on electrolysis.

When an aqueous solution of NaCl is electrolyzed, the discharge potential of the hydrogen ion (H^+) is reached long before that of the sodium ion ($Na^+ \rightarrow Na$; $E_0 = 2{\cdot}71$ volts), so that hydrogen and not sodium is liberated at the cathode. Since these hydrogen ions are produced by the ionization of water—

$$H_2O = H^+ + OH^-$$

it follows that the removal of hydrogen ions in this way must lead to the formation of an equivalent number of hydroxyl ions, so that the solution around the cathode becomes increasingly alkaline. The sodium ions take no part in the reaction. The progressive increase in hydroxyl ion concentration during the electrolysis is accompanied by an equivalent decrease in chloride ions (Cl^-) which are discharged at the anode. The nature of the solution around the cathode therefore changes from sodium chloride (i.e. $Na^+ + Cl^-$) to sodium hydroxide (i.e. $Na^+ + OH^-$). If the anode and cathode solutions are mixed together during the electrolysis, the following reaction occurs—

$$Cl_2 + 2NaOH = NaCl + NaOCl + H_2O$$

With efficient stirring practically all the chlorine reacts in this way, so that it may be said that two faradays of electricity produce one molecular weight of sodium hypochlorite. The resulting sodium hypochlorite may then react in several ways—

(*a*) Reduction may occur at the cathode by the action of the nascent hydrogen liberated there. This reduction may be prevented by the addition of a little potassium chromate. Its action is attributed by Müller to the reduction of the chromate ions to chromic ions, ($CrO_4^{--} \rightarrow Cr^{+++}$), followed by the formation of chromium chromate which forms a film on the cathode and so keeps the bulk of the solution away from the nascent hydrogen.

(*b*) At the anode, the hypochlorite ions are discharged, and then react with the water present to form chlorate ions and liberate oxygen—

$$ClO^- = (ClO) + e$$

$$6(ClO) + 3H_2O = 2ClO_3^- + 6H^+ + 4Cl^- + \tfrac{3}{2}O_2$$

The hydrogen ions (H^+) are neutralized by the hydroxyl ions (OH^-) which accumulate at the cathode. This equation shows that one faraday of electricity is required for the discharge of one hypochlorite gramme-ion, and results in the formation of an equivalent amount of chlorate.

As the electrolysis proceeds, the concentration of sodium hypochlorite increases until it is decomposed in (*b*) as fast as it is formed. Its concentration will then remain steady, and the solution becomes increasingly rich in sodium chlorate.

(*c*) The hypochlorite ions may also react directly with hypochlorous acid which must also be formed in the solution—

$$ClO^- + H^+ = HOCl$$
$$2HOCl + ClO^- = ClO_3^- + 2HCl$$

In weak solutions and at low temperatures, this reaction is slow and has little effect on the course of the electrolysis, especially if the solution is made alkaline. If the solution is made acid, then the reaction becomes important. At 70°C, most of the hypochlorite formed reacts in this way, the ultimate product being almost entirely sodium chlorate.

Properties of Chlorates. They are all powerful oxidizing agents, and form dangerously explosive mixtures with phosphorus, carbon, sulphur, sugar, etc. The dangerous nature of such pyrotechnic compositions cannot be too strongly stated. Explosions may occur on stirring, on warming, or even without externally heating, due to slow oxidation liberating sufficient heat to initiate the explosion.

Potassium chlorate unlike sodium chlorate is only sparingly soluble in cold water, and so may be prepared pure by crystallizing a hot solution. Potassium chlorate is the usual salt of chloric acid to be found in the laboratory, and for this reason, its behaviour may be considered here as representative of those of other chlorates.

On heating, potassium chlorate first melts without decomposition at 370°C and then slowly decomposes by a self-oxidation-reduction reaction to form chloride and perchlorate—

$$4KClO_3 = 3KClO_4 + KCl$$

At higher temperatures, the latter decomposes to form more chloride and liberate oxygen. In the presence of manganese dioxide which acts as a catalyst, the chlorate decomposes directly to the chloride below the melting point and oxygen is liberated—

$$2KClO_3 = 2KCl + 3O_2 \uparrow$$

With concentrated sulphuric acid in the cold, potassium chlorate forms chloric acid, the decomposition of which on warming produces the familiar crackling noise. The student is advised not to attempt this reaction, unless carried out carefully with quite small quantities of chlorate and acid.

With concentrated hydrochloric acid and warming, a mixture of chlorine and chlorine dioxide, known as euchlorine, is evolved, and if a chlorate solution is warmed with a strong solution of sulphur dioxide, it is quantitatively reduced to chloride—

$$4KClO_3 + 16HCl = 4KCl + 2ClO_2\uparrow + 7Cl_2\uparrow + 8H_2O$$

$$KClO_3 + 3H_2SO_3 = KCl + 3H_2SO_4$$

Chlorine Heptoxide, Cl_2O_7, is prepared from its parent acid by dehydration with phosphorus pentoxide. The perchloric acid is added very slowly to phosphorus pentoxide kept at $-10°C$, and after allowing some hours for the dehydration to occur, the chlorine heptoxide is distilled over as a colourless oil, b. p. 82°C.

$$2HClO_4 - H_2O \rightarrow Cl_2O_7$$

Although it is the most stable of the chlorine oxides, it slowly decomposes at ordinary temperatures, and explosively so on heating or on percussion.

Perchloric Acid and Perchlorates. Perchloric acid, $HClO_4$, is prepared as an aqueous solution by the action of concentrated sulphuric acid on potassium perchlorate—

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4$$

Since the acid decomposes on heating, it can only be separated by distillation under reduced pressure, the effect of reducing the pressure being to lower the boiling point. Thus it boils at 14° — 18°C under 15 to 20 mm pressure to form an oily, colourless, fuming liquid which resembles sulphuric acid in its vigorous reaction with water. It is a powerful oxidizing agent and ignites paper or wood, explodes with charcoal, and is liable to decompose explosively on standing.

Perchlorates. Potassium perchlorate may be prepared from potassium chlorate by first cautiously fusing the chlorate, when the following reaction occurs—

$$4KClO_3 = 3KClO_4 + KCl$$

The resulting mixture of potassium chloride and perchlorate is then ground with a little cold water to dissolve up the very much more soluble potassium chloride. This process is repeated to leave the almost insoluble potassium perchlorate, solubility 0·7 per cent at 0°C.

Commercially, potassium perchlorate is prepared by the electrolysis of strong aqueous solutions of sodium chlorate at ordinary temperatures. Sodium perchlorate is first formed by anodic oxidation of the chlorate, and when treated with potassium chloride, precipitates the sparingly soluble potassium perchlorate.

$$NaClO_4 + KCl = NaCl + KClO_4\downarrow$$

Properties. The perchlorates are much more stable than the corresponding chlorates (although they have a higher oxygen content) and are therefore much safer to handle. This accounts for the use of perchlorates but not of chlorates in pyrotechnic compositions and in certain explosives, such as *ophorite*, a composition containing magnesium powder and potassium perchlorate. Potassium perchlorate is a less powerful oxidizing agent than potassium chlorate and does not, for example, oxidize hydrochloric acid or sulphurous acid, nor "crackle" with sulphuric acid.

Potassium perchlorate is one of the least soluble potassium salts and is in fact practically insoluble in alcohol, but other perchlorates are more soluble. Thus strontium perchlorate and barium perchlorate are very soluble in alcohol, and the resulting solutions when ignited burn with a bright crimson flame in the case of the strontium salt, and a green flame in the case of the barium salt.

Magnesium perchlorate is nowadays extensively used as a drying agent in place of phosphorus pentoxide.

Constitution of the Oxides and Oxy-acids of Chlorine

1. It will have been noted from the preceding discussions that the oxygen compounds of chlorine increase in stability with increase in the proportion of oxygen in the molecule, and that the heptoxide and perchlorate are appreciably more stable than the monoxide and hypochlorite. This increase in stability shows that the following structural formulae are incorrect—

$$H—O—Cl;\quad H—O—O—Cl;\quad H—O—O—O—Cl;\quad \text{etc.}$$

since it would mean that the —O—O— chain becomes increasingly stable with increase in the number of oxygen atoms involved. It is only necessary to compare the relative stabilities of water and hydrogen peroxide, to see that the opposite is in fact the case, especially as no compound, such as H—O—O—O—H has ever been isolated.

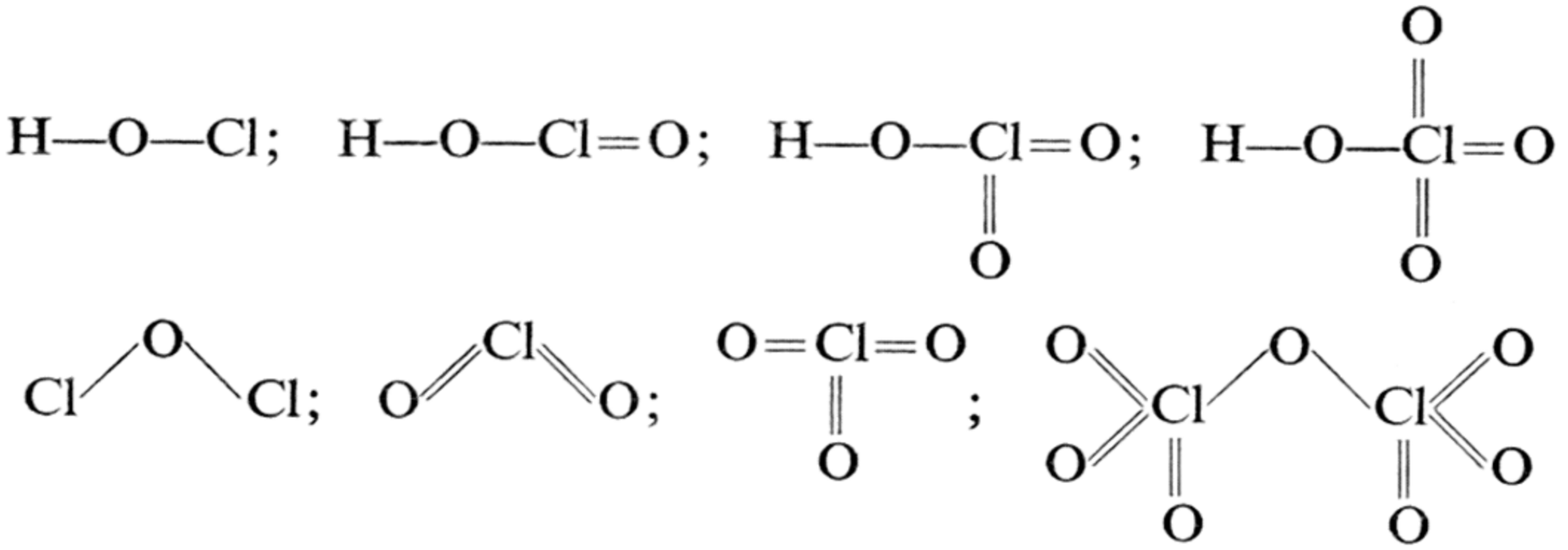
2. The generally accepted structures, until quite recently, have considered the additional oxygen atoms, after hypochlorous acid, to be attached to the chlorine atom by its lone-pairs of electrons, i.e.—

$$H—O—Cl;\quad H—O—Cl\rightarrow O;\quad H—O—Cl(\uparrow O)\rightarrow O;\quad H—O—Cl(\uparrow O,\downarrow O)\rightarrow O$$

The employment of the lone-pairs of electrons on the chlorine atom in forming such co-ordinate linkages would be expected to increase the stability of the molecule as a whole, in agreement with fact. Also, in the proposed formula for perchloric acid, all the lone-pairs of electrons of

the chlorine atom have been used, so that this acid should represent the highest member of the series. This is also in accordance with fact, since no oxy-acid of chlorine containing more oxygen than perchloric acid has yet been isolated.

3. Modern theory considers the co-ordinate link to represent a rather weak bond, and to occur much less frequently than was formerly supposed. The valency of chlorine is accordingly no longer considered to have the constant value of one in its oxy-compounds, and the formulae are now considered to be—



It thus appears, from a study of the chlorine compounds that chlorine shows all valencies from one to seven inclusive (with the exception of two), but the most stable compounds are those in which the valency is either one or seven.

Oxy-compounds of Bromine

Bromine appears to form no oxides stable at ordinary temperatures, but the monoxide, Br_2O, may exist at low temperatures. Hypobromic and bromic acids and salts are analogous both in preparation and behaviour to the corresponding chlorine compounds, but no perbromic acid or perbromate is known.

Potassium bromate on heating forms the bromide and liberates oxygen

$$2KBrO_3 = 2KBr + 3O_2 \uparrow$$

but some bromates, such as magnesium bromate, on heating decompose to the oxide, liberating both oxygen and bromine—

$$2Mg(BrO_3)_2 = 2MgO + 2Br_2 \uparrow + 5O_2 \uparrow$$

Oxy-compounds of Iodine

The oxy-compounds of the halogens do not show quite the same progressive change in properties as has been observed with the other halogen compounds, and this is very largely due to the fact that iodine is predominantly an electropositive element in its compounds. A similar increase in electropositive character with increase in atomic weight occurs in other groups of the Periodic Table, for example, tellurium in Group VI and bismuth in Group V. The relative unimportance of the oxy-compounds

of bromine serves also to emphasize this difference in character between the oxy-compounds of chlorine and of iodine, and it is then less surprising to find that the higher oxy-compounds of iodine are appreciably more stable than the higher oxy-compounds of chlorine.

Iodine Hydroxide, IOH. A very unstable solution of this compound may be prepared by dissolving iodine in cold aqueous alkali, a reaction which recalls the similar behaviour of chlorine and of bromine and suggests that the compound is *hypo-iodous acid*, HOI. Iodine hydroxide is however amphoteric, with the basic properties predominating, but only the salts of this hydroxide with the stronger acids are stable. Thus the following compounds are relatively stable and definitely salt-like in character—ICl, IBr, ICN and IN_3. Iodine hydroxide decomposes on standing to form iodic acid and hydriodic acid, which may then react together to liberate free iodine—

$$3IOH = HIO_3 + 2HI$$
$$HIO_3 + 5HI = 3I_2 + 3H_2O$$

Oxides of Iodine. The principal oxide of iodine is the pentoxide, I_2O_5, but other oxides, such as I_2O_4 and I_4O_9 are also known. These latter are probably not true oxides but the iodate salts of the basic trivalent iodine cation, I^{+++} e.g.—

$I_2O_4 = IO^+ . IO_3^-$, that is, basic iodine iodate;
$I_4O_9 = I^{+++} . (IO_3)_3^-$, that is, normal iodine iodate.

No higher oxide than I_2O_5 is known.

The trivalent iodine normal and basic salts may be considered to be derived from the unstable I_2O_3, a basic oxide. The higher oxide, I_2O_5, however is entirely acidic, and forms the corresponding iodic acid and iodates—

(I_2O_3)—entirely basic→salts, such as ICl_3, $I_2(SO_4)_3$
I_2O_5—entirely acidic→iodic acid, HIO_3, and iodates, KIO_3, etc.

Iodine Pentoxide, I_2O_5. This oxide is obtained as a white solid by the dehydration of iodic acid on heating to about 170°C—

$$2HIO_3 - H_2O = I_2O_5$$

It dissolves in water to re-form iodic acid, and is remarkable in that it is considerably more stable than any other halogen oxide. It decomposes without explosion into iodine and oxygen on heating above 200°C.

Iodic Acid, HIO_3. In general, this is prepared by oxidizing iodine as shown in the first three methods given below—

(1) By oxidizing iodine with concentrated nitric acid—

$$10HNO_3 + I_2 = 2HIO_3 + 10NO_2 + 4H_2O$$

On cooling, crystals of iodic acid separate.

(2) By treating iodine with such oxidizing agents as aqueous chlorine or bromine, hypochlorites or permanganate. Thus, iodic acid is formed when a current of chlorine is passed through a suspension of iodine in water—

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl$$

(3) By warming a solution of chloric acid with iodine—

$$2HClO_3 + I_2 = 2HIO_3 + Cl_2 \uparrow$$

This reaction should be compared with the reaction—

$$2HI + Cl_2 = 2HCl + I_2$$

since it reveals the great difference between iodine and chlorine in their relative affinities for oxygen and hydrogen. Chlorine has the greater affinity for hydrogen (compare relative stabilities of HCl and HI), but iodine has the greater affinity for oxygen (compare relative stabilities of HIO_3 and $HClO_3$).

(4) Iodic acid may also be prepared by the action of dilute sulphuric acid on barium iodate—

$$Ba(IO_3)_2 + H_2SO_4 = BaSO_4 \downarrow + 2HIO_3$$

Iodic acid is a white crystalline solid, which dehydrates on heating at 170°C to form its anhydride, iodine pentoxide. It is soluble in water and a strong oxidizing agent. The reaction with HI has already been noted as an example of its oxidizing action; other examples include its reactions with sulphuretted hydrogen and also with sulphurous acid—

$$5H_2S + 2HIO_3 = 5S \downarrow + 6H_2O + I_2 \downarrow$$
$$5SO_2 + 2HIO_3 + 4H_2O = 5H_2SO_4 + I_2 \downarrow$$

Potassium Iodate may be prepared by the action of iodine on potassium hydroxide (the intermediate unstable iodite decomposing)—

$$3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O$$

or more conveniently, by heating a concentrated solution of potassium chlorate with iodine, and adding a little nitric acid.

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2 \uparrow$$
$$(\text{cf. } 2KI + Cl_2 = 2KCl + I_2)$$

Like the chlorate and bromate, the iodate decomposes on heating, although a somewhat higher temperature is necessary—

$$2KIO_3 = 2KI + 3O_2 \uparrow$$

The reaction of HIO_3 and HI to liberate free iodine is recalled in the use of potassium iodate to standardize sodium thiosulphate solutions. A weighed

amount of the pure iodate is treated with potassium iodide in solution and acidified. The following reaction then occurs quantitatively and the iodine may be titrated against the thiosulphate in the usual way.

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O$$

Periodic Acid. Periodic acid exists not as the normal acid, HIO_4, but as para-periodic acid, H_5IO_6 (or $HIO_4 . 2H_2O$), a deliquescent solid. Normal periodates, such as $NaIO_4$, have been prepared, but the salts most easily formed belong to the latter type. Thus, when sodium iodate and sodium hydroxide are dissolved together in water, and chlorine passed in, the oxygen from the first-formed hypochlorite oxidizes the iodate, and the salt which crystallizes out is the para-periodate, $Na_2H_3IO_6$.

Para-periodic acid may most easily be prepared by heating a suspension of iodine in perchloric acid—

$$2HClO_4 + I_2 + 4H_2O = 2H_5IO_6 + Cl_2$$

Periodic acid is a powerful oxidizing agent, much stronger in fact than iodic acid, but as with the other per-acids of the halogens, the name is a misnomer, since it does not contain the true peroxide grouping, —O—O—.

Interhalogen Compounds. The halogens form a number of compounds with themselves, and include such compounds as—

ClF (gas)	ICl (b. p. 97°C)
ClF_3 (b. p. 12°C)	ICl_3 (m. p. 101°C)
BrF (gas)	
BrF_3 (b. p. 127°C)	IF_5 (b. p. 97°C)
BrF_5 (b. p. 40°C)	IF_7 (b. p. 5–6°, m. p. 4·5°C)

In general, these compounds are formed by direct reaction between the elements, the final product depending on the relative concentrations of reacting halogens. They are all decomposed by water, but IF_7 is the most stable in this respect and is only slowly attacked by water at ordinary temperatures.

General Review of the Chemical Properties of the Halogens

1. General reactivity decreases from fluorine to iodine.
2. Affinity for hydrogen decreases from fluorine to iodine.
3. Affinity for oxygen increases from fluorine to iodine, but the difference in the nature of the oxy-compounds of iodine when compared with those of chlorine is accentuated by the relative scarcity and unimportance of the oxy-compounds of bromine and by such reactions as

$$2HClO_3 + I_2 = 2HIO_3 + Cl_2$$

In general the most stable oxy-compounds of each halogen are those containing the most oxygen.

4. Gradual change in electrochemical character from fluorine to iodine. Fluorine is the most electronegative of all elements; iodine is predominantly electropositive in its compounds and thus shows an abrupt change from the other halogens.

5. Anomalous properties of fluorine (*see* p. 780) when compared with the other halogens, reveals a closer similarity in the properties of this element to oxygen.

Some of these points of similarity are collected together in the following short Table.

TABLE 108

Fluorine Compared with Chlorine and Oxygen

Chlorine	Fluorine	Oxygen
HCl, *gas*, dissolves in water to form a *strong* acid	H_2F_2, *liquid*, dissolves in water to form a *weak* acid	H_2O, *liquid*, neutral
Good conductor of electricity	Non-conductor but *good* ionizing solvent	Poor conductor but *good* ionizing solvent
Non-associated	Associated, H_2F_2	Associated, $(H_2O)_n$
Does not react directly with carbon	Reacts directly with carbon $\rightarrow CF_4$	Reacts directly with carbon $\rightarrow CO_2$
Does not form compounds in which the other element shows its maximum valency; e.g. SCl_6 not stable	IF_7, SF_6 and OsF_8, all stable compounds	SO_3, OsO_4, all stable compounds
$CaCl_2$, soluble AgCl, insoluble	CaF_2, insoluble AgF, soluble	CaO, insoluble, (but reacts with water $\rightarrow Ca(OH)_2$)

Uses of Chlorine, Bromine and Iodine

Chlorine finds its main use as a bleaching agent (in the form of bleaching powder, sodium hypochlorite and sodium chlorite) for linen and cotton goods, wood-pulp and paper. It is also used in the manufacture of such compounds as chloroform, trichlorethylene and carbon tetrachloride in addition to the other compounds described in the present chapter (e.g. hydrochloric acid). It is also used to sterilize water for drinking purposes and also in the treatment of sewage and swimming-bath water.

Bromine is used for such purposes as the manufacture of photographic

films and plates (AgBr), of various organic dyestuffs and chemo-therapeutic agents, in metallurgy and also in recent years in the preparation of anti-knock motor-fuels containing lead tetra-ethyl and ethylene dibromide.

The main uses of *iodine* are in the medical field, some 70 per cent of the world production being used for this purpose. The medical uses of iodine may be divided into—

(*a*) Solutions of iodine, for example in alcohol (known as *tincture of iodine*) or in aqueous potassium iodide, which are used for their germicidal action. In this connexion it is worth noting that the latter solution is a more effective germicide than the "tincture."

(*b*) Salts, such as potassium iodide, which are frequently administered internally for treatment of goitre, syphilis, etc.

(*c*) Organic compounds containing iodine which are used as chemo-therapeutic agents in the treatment of dysentery, leprosy and arthritis, and also as contrast media in X-ray radiographic examination of the human system.

Industrial applications of iodine include its use in the manufacture of organic dyestuffs; in photography (especially infra-red); in "Polaroid," a light-polarizing material which is used in anti-dazzle motor-car headlights, protective sunglasses and various polarizing instruments; in the manufacture of heat-sensitive paints containing copper, mercury and silver iodides; and in many other less important connexions.

MANGANESE

Occurrence. Manganese does not occur free in nature and most of the world's supply is obtained from the two black minerals, *pyrolusite*, MnO_2 and *psilomelane*, an impure hydrated oxide with or without varying amounts of barium and potassium. These minerals may be accompanied by other black oxides such as *wad* or "bog manganese," *braunite*, Mn_2O_3, and *manganite*, $Mn_2O_3 . H_2O$, the carbonate, *rhodochrosite* (*dialogite*), $MnCO_3$, and the silicate, *rhodonite*, $MnSiO_3$ which are pink in colour and are not of commercial importance unless they have been oxidized to one of the black oxides.

The chief deposits of manganese ores are found at Nikopol in the Ukraine, Chiaturi in the Caucasus, the Gold Coast, Brazil and India.

Extraction of Manganese. Manganese is manufactured by the following processes.

(*a*) *The Goldschmidt Process* in which manganomanganic oxide, Mn_3O_4, is used as the source of manganese, the aluminium powder being incorporated with the oxide; the reaction involved is—

$$3Mn_3O_4 + 8Al = 4Al_2O_3 + 9Mn$$

(*b*) *Electrolytic Process* in which a concentrated solution of manganous chloride is used as electrolyte and mercury as the cathode. The manganese

forms an amalgam with the mercury and the latter metal is subsequently distilled off by heating to a temperature of 250°C, under vacuum.

(*c*) *Thermal Reduction by Carbon.* Manganese, containing carbon as an impurity is obtained by the thermal reduction of the dioxide with carbon in an electric furnace. When less than the theoretical quantity of carbon is employed, manganese metal of considerable purity is obtained. Two typical analytical ranges of such manganese are quoted below.

TABLE 109

Typical Analytical Ranges of Manganese produced by Thermal Reduction

Sample	Mn	Fe	C	Si
	Percentage			
Manganese metal (*A*) . .	95–98	1–3	0·3 max	1·5 max
Manganese metal (*B*) . .	85–90	2 max	7·0 max	3·0 max

(*d*) *Ferromanganese Production.* Large quantities of manganese are produced in the form of ferro alloys by smelting mixed ores of manganese and iron. Thus ferromanganese contains 78–82 per cent Mn along with 3–7 per cent C, the balance being made up of iron. A refined ferromanganese is also made containing 80–85 per cent Mn, 0·1–2 per cent C, and up to 2 per cent Si. *Spiegeleisen* contains 26–28 per cent Mn, 5 per cent C, and a maximum of 1 per cent Si, the balance being iron. In addition to these materials there are also produced for special purposes silicomanganese containing 65–75 per cent Mn, and 14–25 per cent Si, and silicospiegel with 25–30 per cent Mn, and 7–10 per cent Si. The balance is iron in each case.

Physical Properties of Manganese

(*a*) Pure manganese is a silvery-white metal, although the impure metal often exhibits a slightly red or yellowish tinge.

(*b*) It is very hard and brittle, readily scratching glass and not being marked by a file.

(*c*) It has a high melting point (1242°C) and a high boiling point (2151°C).

(*d*) Manganese may exist in various polymorphic modifications according to the temperature of the observation. Thus, up to 742°C, manganese occurs in the form of body-centred cubic structure—this is α-manganese; from 742°–1191°C, β-manganese occurs having another cubic type of structure; whilst from 1191°C, to the melting point there exists γ-manganese having a tetragonal face-centred structure. It should also be noted that

electrolytic manganese also occurs in this latter tetragonal form. These polymorphic changes are of considerable importance in the metallurgy of manganese steels.

(*e*) Manganese has a high density, 7·44.

Chemical Properties of Manganese

(*a*) Pure manganese is not attacked either by the atmosphere or by water, although when heated it combines readily with such elements as carbon, nitrogen, the halogens and boron. As obtained commercially, however, manganese suffers a slight superficial attack when exposed to the air, and is attacked by water, thus—

$$Mn + 2H_2O = Mn(OH)_2 + H_2 \uparrow$$

(*b*) Manganese is readily attacked by all the ordinary dilute acids, inclusive of acetic acid, evolving hydrogen copiously and forming the corresponding manganous salts.

(*c*) Above 330°C, manganese is oxidized by carbon monoxide.

(*d*) At elevated temperatures it exhibits considerable affinity for sulphur and for oxygen; these facts are of considerable importance in the metallurgy of iron and steel in connexion with the deoxidation and the desulphurization of iron.

Uses of Manganese. The chief uses of metallic manganese are in connexion with the production of alloys.

In the production of ferrous alloys, manganese is used in the form of ferromanganese, spiegeleisen, etc., for the deoxidation and the desulphurization of iron and of steel. These alloys are also employed when it is desired to produce irons and steels of higher manganese contents; it should be noted here that all steels and cast irons contain up to approximately 0·6 per cent manganese and it is only when this figure is exceeded that the materials known as manganese steels and alloy cast irons are produced. The former of these two materials are used for general engineering structural applications when the manganese content is of the order of 1·5 per cent; these materials are the so-called "pearlitic manganese steels"; the "austenitic manganese steels" contain 12–14 per cent manganese and exhibit a very high surface hardness, being particularly suitable for such purposes as jaw-crushers and railway cross-overs, etc. Alloy cast irons containing appreciable contents of manganese are employed for the manufacture of engineering components which must exhibit high resistance to abrasion.

Manganese is less common in non-ferrous alloys than in ferrous alloys. A copper alloy containing 8–12 per cent Mn, 4 per cent Ni, the balance being copper is employed for the manufacture of electrical resistances; whilst manganese bronze (high-tensile brass) is of considerable importance both in cast form as well as in wrought form; it contains up to 3·5 per cent Mn. Manganese is employed as a minor addition in a number of

aluminium-base light alloys in which it enhances the mechanical strength, and in certain magnesium-base light alloys in which it enhances the resistance to corrosion.

Compounds of Manganese

Manganese exhibits a large number of valencies, these are enumerated below.

TABLE 110

Valency States of Manganese

Valency	Corresponding Oxide	Corresponding Ion
2	MnO Manganous oxide	Mn^{++} Manganous ion
3	Mn_2O_3 Manganic oxide	Mn^{+++} Manganic ion
4	MnO_2 Manganese dioxide	MnO_3'' Manganite ion
6	MnO_3 Manganese trioxide	MnO_4'' Manganate ion
7	Mn_2O_7 Manganese heptoxide	MnO_4' *Per*manganate ion

The most important of these oxidation states are 2, 4 and 7 respectively. As the valency increases from 2 to 7 the character of the corresponding oxides changes from strongly basic to strongly acidic.

Divalent Manganese Compounds

Manganous Oxide, MnO, may be obtained from any of the other oxides by heating them in a current of hydrogen or by calcining the carbonate. It is a greenish powder which oxidizes rapidly on exposure to the atmosphere.

Manganous Hydroxide, $Mn(OH)_2$, is a pink coloured precipitate produced when an alkali is added to a solution of a manganous salt. It is rapidly oxidized on exposure to the air, turning brown in the process, owing to the formation of manganese trioxide.

Manganous Carbonate, $MnCO_3$, is a reddish precipitate formed by the addition of alkaline carbonates to manganous salts.

Manganous Sulphide, MnS, is a flesh-coloured gelatinous precipitate produced in alkaline solutions by the addition of alkaline sulphides.

Manganous Chloride, $MnCl_2$, and **Manganous Sulphate,** $MnSO_4$, are pink coloured salts produced by the action of the appropriate acid on metallic manganese, manganous oxide, manganous hydroxide, or manganous carbonate.

Trivalent Manganese Compounds

Manganic Oxide, Mn_2O_3, occurs in nature as braunite; it may be produced by heating manganese dioxide in a current of ammonia—

$$6MnO_2 + 2NH_3 = 3Mn_2O_3 + N_2\uparrow + 3H_2O$$

Manganic oxide is a weakly basic oxide which forms the manganic series of salts. In acid solution manganic salts tend to become reduced to the manganous state, and whilst remaining unreduced in solution they are subject to hydrolysis which results in the separation of *manganic hydroxide*, $Mn(OH)_3$.

Mangano-manganic Oxide, Mn_3O_4, may be regarded as made up of manganous and manganic oxides; it dissolves in sulphuric acid, for example to form a solution containing manganous and manganic sulphates.

$$Mn_3O_4 + 4H_2SO_4 = MnSO_4 + Mn_2(SO_4)_3 + 4H_2O$$

Mangano-manganic oxide is formed when any of the other oxides of manganese is heated strongly in the air.

Tetravalent Manganese compounds

Manganese Dioxide, MnO_2, occurs in nature as pyrolusite; it is a black powder which is insoluble in water, but capable of reacting with acids to form salts of tetravalent manganese such as *manganese tetrachloride*, $MnCl_4$, and with bases to form salts such as *calcium manganite*, $CaMnO_3$. It is, therefore an amphoteric oxide. Manganese dioxide is unstable at high temperatures yielding its oxygen to compounds capable of being oxidized at elevated temperatures; it is, therefore, employed as a decolorizing agent in the manufacture of glass since it discharges the green colour of ferrous silicates by forming the less highly coloured ferric silicate. The pale yellow colour of this latter compound is masked by the slight violet colour of the manganic silicate produced.

Although manganese dioxide will itself yield oxygen when heated strongly it is usually employed as a catalyst to promote the evolution of oxygen from such compounds as potassium chlorate. When manganese dioxide is heated with sulphuric acid it yields oxygen at 140°C—

$$4MnO_2 + 6H_2SO_4 = 2Mn_2(SO_4)_3 + 6H_2O + O_2\uparrow$$

At higher temperatures manganous sulphate is formed instead of manganic sulphate—

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2\uparrow$$

The oxidizing action of manganese dioxide is further illustrated by its action on hot concentrated hydrochloric acid.

$$MnO_2 + 4HCl = MnCl_2 + Cl_2\uparrow + 2H_2O$$

This last reaction may be employed as a means of evaluating the content of available oxygen in a sample of pyrolusite, the liberated chlorine being passed through potassium iodide solution and the displaced iodine then determined volumetrically by means of sodium thiosulphate solution.

Another method for the evaluation of pyrolusite depends upon the fact

that when manganese dioxide is heated with concentrated sulphuric acid and oxalic acid, the latter is oxidized to carbon dioxide; it is therefore possible, starting with a known volume of oxalic acid, to determine the excess left behind by titration with standard potassium permanganate solution.

$$MnO_2 + (COOH)_2 + H_2SO_4 = MnSO_4 + 2CO_2\uparrow + 2H_2O$$

In addition to being employed for the decolorizing of glass, manganese dioxide finds very important application as a depolarizer in the manufacture of dry batteries and as a drier in the manufacture of paints. Much of the dioxide is also used in the production of permanganates.

Hexavalent Manganese Compounds

The Manganates. Whilst *manganic acid*, H_2MnO_4 is unknown, salts of this acid are known, and those of the alkaline elements are stable in a state of alkaline fusion. The manganates are bright green in colour and in some cases are isomorphous with the sulphates, the selenates and the chromates. Thus *sodium manganate*, Na_2MnO_4, is prepared by fusing sodium peroxide with sodium hydroxide and manganese dioxide.

$$2MnO_2 + 4NaOH + \underset{\substack{\text{from}\\\text{oxidizing}\\\text{agent}}}{O_2} = 2Na_2MnO_4 + 2H_2O$$

On extraction with water a green solution of sodium manganate is obtained. If this solution is diluted or rendered acidic it will be converted into the violet coloured permanganate, $NaMnO_4$. In this oxidation from the hexavalent to the heptavalent state the oxidizing agent is the manganate ion itself which is itself in part reduced, producing manganese dioxide.

$$3Na_2MnO_4 + 2H_2O \rightleftharpoons 2NaMnO_4 + MnO_2\downarrow + 4NaOH$$

Heptavalent Manganese Compounds

Manganese Heptoxide, Mn_2O_7, is a heavy, violet-brown oily liquid produced when potassium permanganate is added to ice-cold concentrated sulphuric acid. Manganese heptoxide is a very unstable substance liable to explosive decomposition into oxygen and manganese dioxide. Permanganic acid, itself, $HMnO_4$, is stable in acid solution being produced by decomposing barium permanganate with sulphuric acid, which removes the barium as its insoluble sulphate.

The two most important of the permanganates are those of potassium and sodium; they are prepared by first of all making the corresponding manganates by fusion of the appropriate alkali with manganese dioxide. The fused mass is then leached with water and by the process of self-oxidation, as described above, the permanganate is produced. This hydrolysis is assisted meanwhile by passing carbon dioxide through the

solution, thereby converting the caustic alkali into the bicarbonate; the violet coloured solution of the permanganate is then filtered through glass wool, concentrated and allowed to crystallize.

Sodium and potassium permanganate are also manufactured by the electrolytic oxidation of the corresponding manganate solutions.

Potassium Permanganate, $KMnO_4$, the most important permanganate, crystallizes in the form of deep violet coloured prisms which dissolve readily in water to produce a magenta coloured solution characteristic of the permanganate ion. Potassium permanganate is a powerful oxidizing agent, thus when heated alone, or with dilute sulphuric acid or with concentrated alkali solution it yields oxygen—

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2\uparrow$$
$$4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2\uparrow$$
$$4KMnO_4 + 4KOH = 4K_2MnO_4 + 2H_2O + O_2\uparrow$$

Potassium permanganate explodes when heated with concentrated sulphuric acid. With hydrochloric acid, potassium permanganate yields chlorine as follows—

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2\uparrow$$

Similarly, sulphites are oxidized by permanganate to sulphates, and nitrites to nitrates.

In solution potassium permanganate behaves as an oxidizing agent in one of two ways according as to whether the solution is either (*a*) acidic, or (*b*) neutral or basic. In acid solution the permanganate ion accepts five electrons to form the manganous ion—

$$MnO_4' + 5e' + 8H^+ \rightarrow Mn^{++} + 4H_2O$$

Typical reactions of this type are as follows—

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$
$$5(COOH)_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2\uparrow + 8H_2O$$
$$10KI + 2KMnO_4 + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$$

In neutral or in alkaline solution the permanganate ion accepts three electrons to form a precipitate of manganese dioxide—

$$MnO_4' + 3e' + 4H^+ \rightarrow MnO_2\downarrow + 2H_2O$$

Thus, under such conditions potassium iodide is oxidized to iodate as follows—

$$KI + 2KMnO_4 + H_2O = KIO_3 + 2KOH + 2MnO_2\downarrow$$

CHAPTER 26

THE ELEMENTS OF GROUP VIII

IRON

Occurrence. Apart from occasional specimens of metallic iron, this metal always occurs in nature in the form of compounds, the most common of which are oxides, carbonates and sulphides. The first two groups of these compounds are by far the most important, and it is from them that the world's supply of iron is obtained.

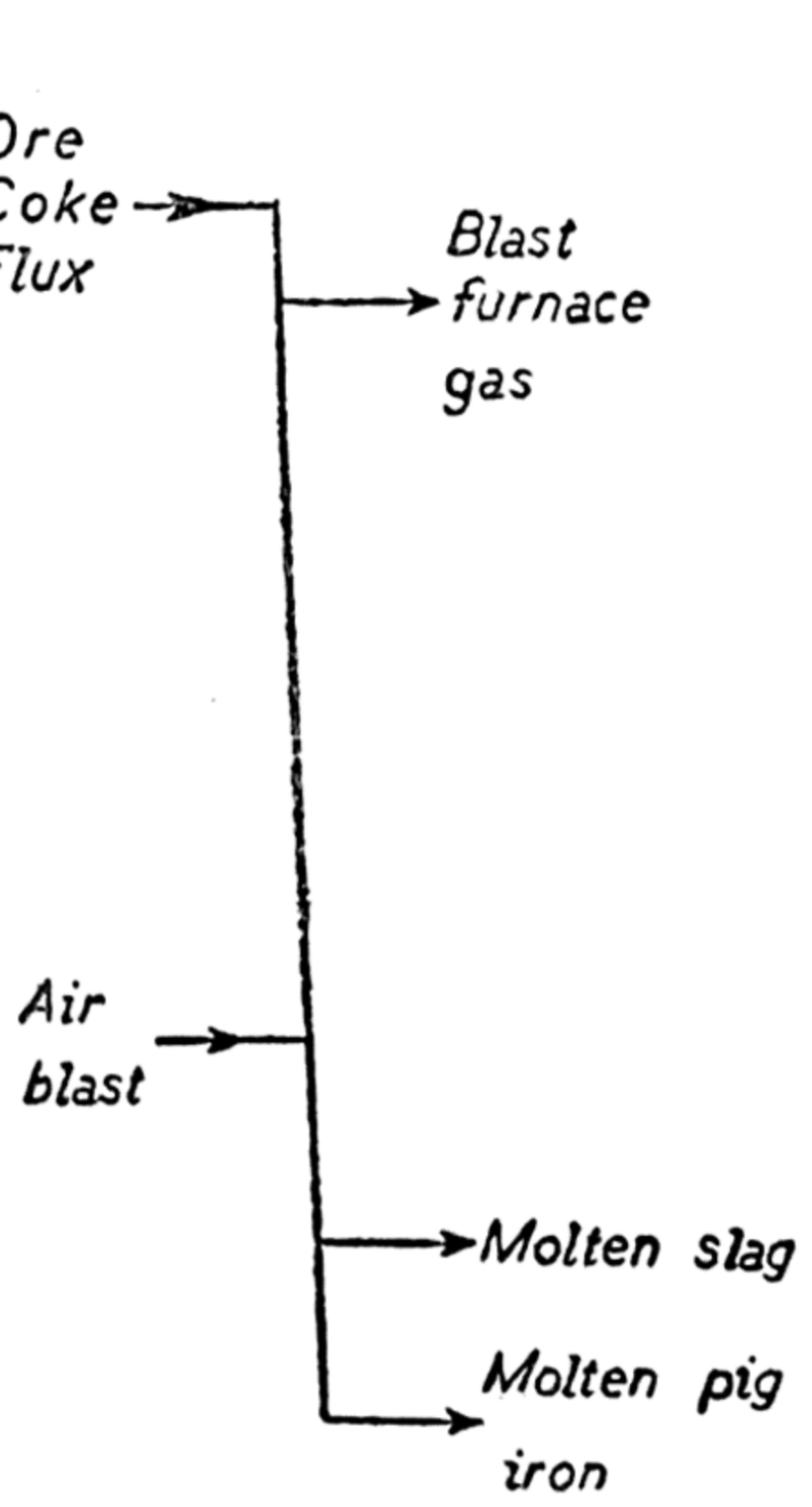
The ores of iron may be divided into two groups: (*a*) high phosphorus ores, and (*b*) low phosphorus ores. Since practically all the phosphorus in the charge passes into the pig iron produced during the smelting process, this distinction is obviously important. The carbonate and hydrated oxide ores such as *clay ironstone*, *black band iron ore*, *spathose*, and certain of the *brown hæmatites* or *limonites* which in Great Britain are found principally in Lincolnshire, Northamptonshire, Staffordshire and Lanarkshire, are of the high phosphorus type, and it is from these ores that the so-called "basic pig irons" are smelted. The iron content of such ores varies from about 20 per cent in the case of clay ironstone to approximately 60 per cent for limonite. The low phosphorus ores are all oxide ores of which the chief are *magnetite* (*magnetic iron ore* or *lodestone*) containing ferroso-ferric oxide, Fe_3O_4, and mined principally in Scandinavia, North America and India; and *red hæmatite* (*kidney iron ore* or *specular iron ore*) containing ferric oxide, Fe_2O_3, deposits of which occur in the Carnforth district of Lancashire, the Santander and Bilbao districts of Northern Spain, and the Lake Superior region of North America. Good samples of magnetite contain about 72 per cent iron, and red hæmatite approximately 70 per cent iron.

In addition to the above mentioned ores, sintered pyritic ores known as "*Blue Billy*" or *purple ore*, *cinder* from reheating and puddling furnaces, and *forge scale* also constitute part of the blast furnace charge in certain plants.

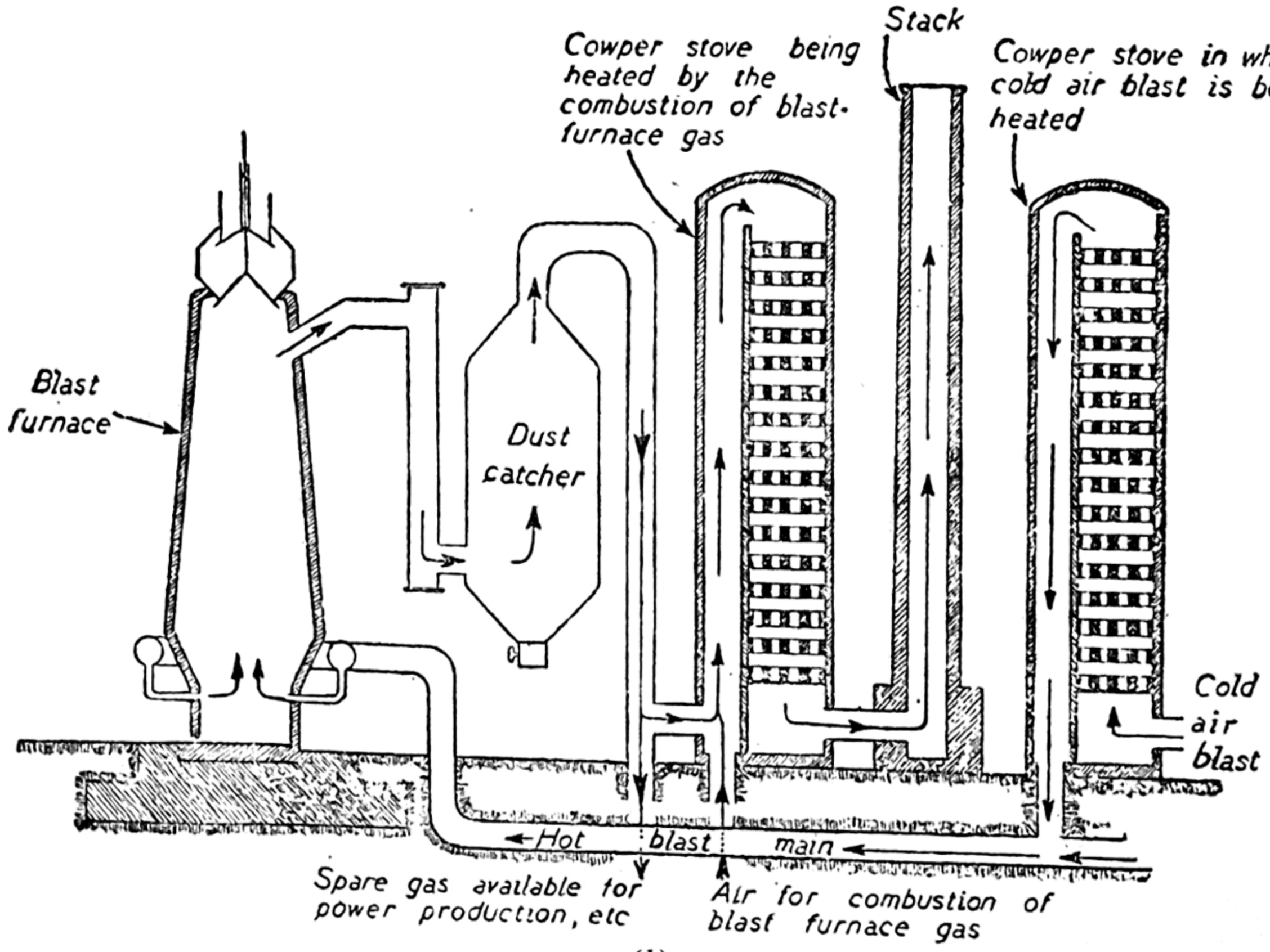
Extraction of Iron. This is achieved in two stages, (i) calcination of the iron ore, and (ii) smelting.

Calcination. Before an iron ore is charged into the blast furnace it is necessary, in most cases to subject the material to a preliminary process. This consists in the first instance of ore dressing to remove as far as possible the gangue or "vein stuff."

The concentrate from this preliminary treatment is then calcined or heated in a special type of kiln in order to ensure that any ferrous oxide is



(*a*)



(*b*)

FIG. 250. (*a*) Flowsheet Through Blast Furnace, (*b*) General Arrangement of Blast Furnace and Subsidiary Plant

converted to ferric oxide, and also that any manganese present exists in its highest state of oxidation. In addition to these chemical changes, calcination causes the material to assume a more porous state, thus making for more ready reduction to metallic iron in the blast furnace, and it lowers the sulphur content.

Smelting in the Blast Furnace. The calcined ore is then charged into the blast furnace along with coke and limestone, the ore and the limestone constituting what is known as the "burden." The movement of these materials through the blast furnace is shown in the form of a flow sheet in Fig. 250(*a*), whilst the general arrangement of the blast furnace and its subsidiary plant is given in Fig. 250(*b*).

The blast furnace consists of a tapered, cylindrical steel shell, lined with refractory brickwork and in most cases of a total height of about 100 ft. Air is preheated in Cowper stoves to a temperature of about 650°C and blown into the lower part of the blast furnace through *tuyeres*, so causing the coke to burn principally to carbon monoxide which passes upwards through the furnace, reducing the iron oxide to metal, thus—

$$Fe_2O_3 + 3CO = 3CO_2 \uparrow + 2Fe$$

The reduced iron, which remains in the form of a spongy mass, on descending still further, melts and runs down to the well or hearth of the furnace, whence it is tapped off at regular intervals.

Concurrently with the reduction of the iron oxide, the gangue and flux react with one another, and later with the coke ash, to produce a readily fusible slag or cinder which floats on the surface of the heavier molten iron and is tapped from the furnace through a slag notch situated higher in the well than the iron notch, this reaction being as follows—

$$2CaO + 2SiO_2 = 2CaO \,.\, SiO_2$$

The waste gases which pass upwards through the blast furnace consist of about 30 per cent CO and 10 per cent CO_2, the remainder being largely nitrogen; this mixture is known as *blast furnace gas*. To prevent the escape of the blast furnace gas during charging, two conical bells are fitted to the top of the blast furnace; these operate as follows. The charge in the skip is delivered to the upper bell which is then lowered to allow the charge to fall on to the lower bell, which meanwhile is held against its hopper, so preventing the escape of gas; the upper bell is then raised and the lower bell lowered, so permitting the entrance of the charge into the furnace but precluding the escape of gas, all of which passes along the downtake. The products of the blast furnace are therefore *pig iron*, *slag* and *gas*. *Blast furnace slag* is used in the manufacture of slag wool, a material valuable for its thermal and acoustical insulating properties, for making certain types of cements, and for road metal and railway ballast. The *blast furnace gas*, after cleaning, is used for many purposes amongst

which may be mentioned the heating of the Cowper stoves in which the gas is burnt with sufficient air for combustion, and for steam raising in boilers fitted with gas burners instead of the usual grate, as fuel for gas engines driving blowers to supply the large volume of air required in the blast furnace, for mixing with coke-oven gas as a fuel in open-hearth steel furnaces and reheating furnaces, and to a certain extent for illuminating purposes.

For a modern blast furnace using red hæmatite ore and producing 750 tons of iron per day the following materials are required—1250 tons ore, 700 tons coke, 290 tons limestone, and 2500 tons air; in addition to the pig iron produced, 75 million cubic feet of blast furnace gas will be produced daily.

The molten iron as tapped from the blast furnace may be used either for the manufacture of steel by transferring it in the molten state to the steel works, or it may be cast into rough bars or *pigs*, from 36 in. to 48 in. long and weighing from 1 to $1\frac{3}{4}$ cwt each. This is the *pig iron* of commerce.

The casting of pig iron may be carried out either intermittently by running the iron straight from the blast furnace into prepared open sand moulds, or continuously by means of a pig-casting machine consisting of one or more endless rotating belts in which iron moulds are mounted; the molten iron is run from a ladle into the moulds at one end of the rotating belt and the pigs so formed are rapidly chilled by water sprays as the belt moves on, until at the other end of the cycle, they are quite solid and suitable for charging direct into the waiting trucks. These machine-cast pigs are usually supplied in the form of slabs weighing about 1 cwt.

Classification of Pig Irons and Their Uses. If the temperature of the air used in the blast furnace is not over 100°C, the resulting pig iron is known as *cold-blast pig iron*. The quantity of this material produced is much smaller than that produced using hot blast, and is employed amongst other purposes for the manufacture of high-duty castings. With pre-heated air, *hot-blast pig iron* results, of which there are a number of varieties according to their phosphorus contents; the pig iron with the lowest phosphorus content is that obtained by the smelting of magnetite and red hæmatite, and the highest is basic pig iron. The former of these hot-blast pig irons is employed for the manufacture of high-duty iron castings, for ingot mould castings, and for tinplate manufacture; basic pig irons are employed for the production of basic steel and for the manufacture of general iron castings—in the latter case they are often termed "special" cylinder irons. Pig iron always contains carbon, silicon, sulphur, phosphorus and manganese; the carbon may exist in two forms, as free graphite, and as iron carbide, Fe_3C (cementite). The relative proportions of graphite and iron carbide vary according to the conditions which obtain during manufacture (e.g. blast furnace temperature). When the

graphite content is high the fracture of the pig iron exhibits a grey appearance whilst when the iron carbide content is high the fracture is white in appearance. Pig irons of the high-graphite type are termed *grey pig irons* and those of the high iron carbide type are known as *white irons*. When the graphite content is high the iron carbide content is low, and vice versa. The chief characteristics of grey and white pig irons are tabulated below.

TABLE 111

Chief Characteristics of Grey and White Pig Irons

Grey Pig Iron	White Pig Iron
Most of the carbon is free in the form of graphite	Most of the carbon is chemically combined in the form of iron carbide, Fe_3C
The silicon content is high	The silicon content is low
The manganese content is high	The manganese content is low
The iron is open-grained	The iron is close-grained
The iron is soft and tough	The iron is hard and brittle

In all pig irons the graphite content varies from a trace up to about 3·5 per cent, whilst the iron carbide content varies from about 0·1 to about 3·0 per cent. The silicon content of all pig irons varies from 0·3 to 3·0 per cent, and the manganese content from 0·3 to about 1·4 per cent. In all pig irons the sulphur content ranges from 0·015 to 0·2 per cent. In hæmatite pig irons the phosphorus content ranges from 0·02–0·05 per cent, but in basic pig irons it is usually of the order of 1·4–1·6 per cent.

The Manufacture of Steel

Steel is essentially an alloy of iron with carbon, the content of the latter element varying from about 0·1 to about 1·5 per cent. In addition to carbon, however, there are always present to a greater or less extent the elements silicon, manganese, sulphur, and phosphorus, and in the case of the alloy steels, such elements as nickel, chromium, etc., in addition. It is thus possible to distinguish between (*a*) the so-called "carbon steels"—those not containing alloying elements such as nickel and chromium, nor the elements silicon or manganese in contents over 1 per cent, and (*b*) the so-called "alloy steels" when these composition requirements do not obtain.

In addition to classifying steels according to their chemical composition it is also customary to classify steels as either "acid" or "basic," these names indicating the chemical nature of the furnace lining in which the steel is made. Acid furnace linings are those which are essentially siliceous in nature, whilst basic furnace linings are composed of basic refractories such as calcined dolomite.

The pig iron most suitable for the production of acid steel is that produced from low-phosphorus ores such as red hæmatite; those ores of the high-phosphorus type such as the carbonate ores are only suitable for treatment in basic-lined furnaces and thus give rise to the basic steels. The chief types of steelmaking processes in use at the present time are (*a*) the Bessemer process, (*b*) the open-hearth process, and (*c*) electric processes.

The Bessemer Process. The principle of the Bessemer process consists in blowing air through molten pig iron contained in an egg-shaped vessel known as a *converter*. The converter (*see* Plate VI) consists of a steel shell lined with refractory material which may be either acidic (i.e. siliceous) or basic (i.e. dolomitic) in nature, thus giving rise to two variants of the Bessemer process, (i) the acid Bessemer process, and (ii) the basic Bessemer process, the former being employed with low-phosphorus pig irons, and the latter with high-phosphorus pig irons.

An air blast from a blower is supplied to a blast box situated in the base of the converter, from which air passes to the interior of the converter by way of a large number of holes or tuyeres. The oxygen in this air oxidizes the impurities (i.e. C, Mn, Si, S and P) present in the pig iron which are removed as oxides either in the gaseous state or as constituents of the slag. The siliceous nature of the lining of a converter used in the acid process does not permit of the removal of phosphorus hence the necessity for employing pig irons containing low phosphorus in this variant of the Bessemer process; a basic lining, such as one made of dolomite, renders possible the easy removal of phosphorus.

The converter, already hot from a previous blow or alternatively heated by means of a fire when starting work for the day, is charged with molten pig iron whilst in the horizontal position. The blast is turned on and the converter turned into a vertical position. The process of oxidation which follows causes the liberation of a large quantity of heat, in fact the silicon, manganese, and in the basic process the phosphorus in addition, constitute what are known as "inorganic fuels." The various stages of the "blow" cause alteration in the character of the flame issuing from the mouth of the converter, and it is by observation of this flame that the operator knows from experience whether or not the iron has been fully converted into steel. In the first or "slag-forming" stage during which silicon and manganese are largely oxidized a short luminous flame issues from the converter; but as the content of these elements is reduced the carbon

begins to oxidize to carbon monoxide which burns at the mouth of the converter; this stage, which is accompanied by the ejection of white-hot slag particles, is known as the "boil." With the removal of carbon the flame drops, and this is an indication, when handling low-phosphorus pig iron, that conversion into steel is complete, whereupon the converter is turned down, the blast turned off and the steel poured into the waiting ladle. The average time for a complete blow of acid steel is from 18 to 20 minutes. In the case of high-phosphorus pig irons blowing is continued for 3 to 5 minutes longer after the "drop" of the flame, indicating carbon removal, in order to eliminate phosphorus; this additional period is known as the "afterblow."

The steel poured into the ladle from the converter, however, contains too little carbon for most purposes, and the presence of iron oxide (iron is obviously oxidized to some extent along with the elements carbon, silicon, manganese, sulphur and phosphorus) renders it useless for engineering purposes since in this state it is too brittle. It is, therefore, necessary to deoxidize the steel by making additions to the ladle of ferromanganese or of spiegeleisen (*see* p. 818). The manganese present in these alloys reacts with the iron oxide forming manganese oxide which is removed in the slag. An excess of manganese over and above that required for this deoxidation is always added, and this alloys with the steel, of which it is an essential constituent. A measured addition of anthracite dust is also added to recarburize the steel.

The Open-hearth Process. The principle of the open-hearth process consists essentially in the oxidation of the impurities present in the pig iron, the process being conducted in a shallow bath by means of solid oxidizing agents. The chemical reactions which occur are similar to those occurring in the Bessemer process.

The open-hearth furnace (*see* Fig. 251) consists of a rectangular, double-ended, gas-fired reverberatory furnace. The chamber or hearth in which the gaseous fuel burns connects at each end with regenerator chambers filled with chequer brickwork in a similar manner to that present in Cowper stoves (*see* p. 827). These chequers are worked in pairs, one for gas (a mixture of blast furnace gas and coke-oven gas is often employed), and the other for the air to supply the necessary oxygen for combustion of the gas. Air and gas are passed through each pair alternately, the change-over from one pair to the other taking place at regular intervals of about 20 to 30 minutes. Thus, one pair of regenerators is being heated up by the passage of the hot products of combustion from the hearth to the stack, whilst air and gas are being pre-heated to a temperature of between 900° and 1200°C in the other pair; this will be clear from a study of Fig. 251. The time required for conversion of the charge into steel is from 4 to 10 hours. The lining of the open-hearth furnace, like the Bessemer converter, may be either of acid or of basic refractory

material. Deoxidation is carried out on the steel in the ladle, as tapped from the open-hearth furnace, as in the case of the Bessemer process.

Electric Steel-making Processes. The electric furnaces employed for the manufacture of steel may be divided into two types: (i) arc furnaces, and (ii) high-frequency induction furnaces.

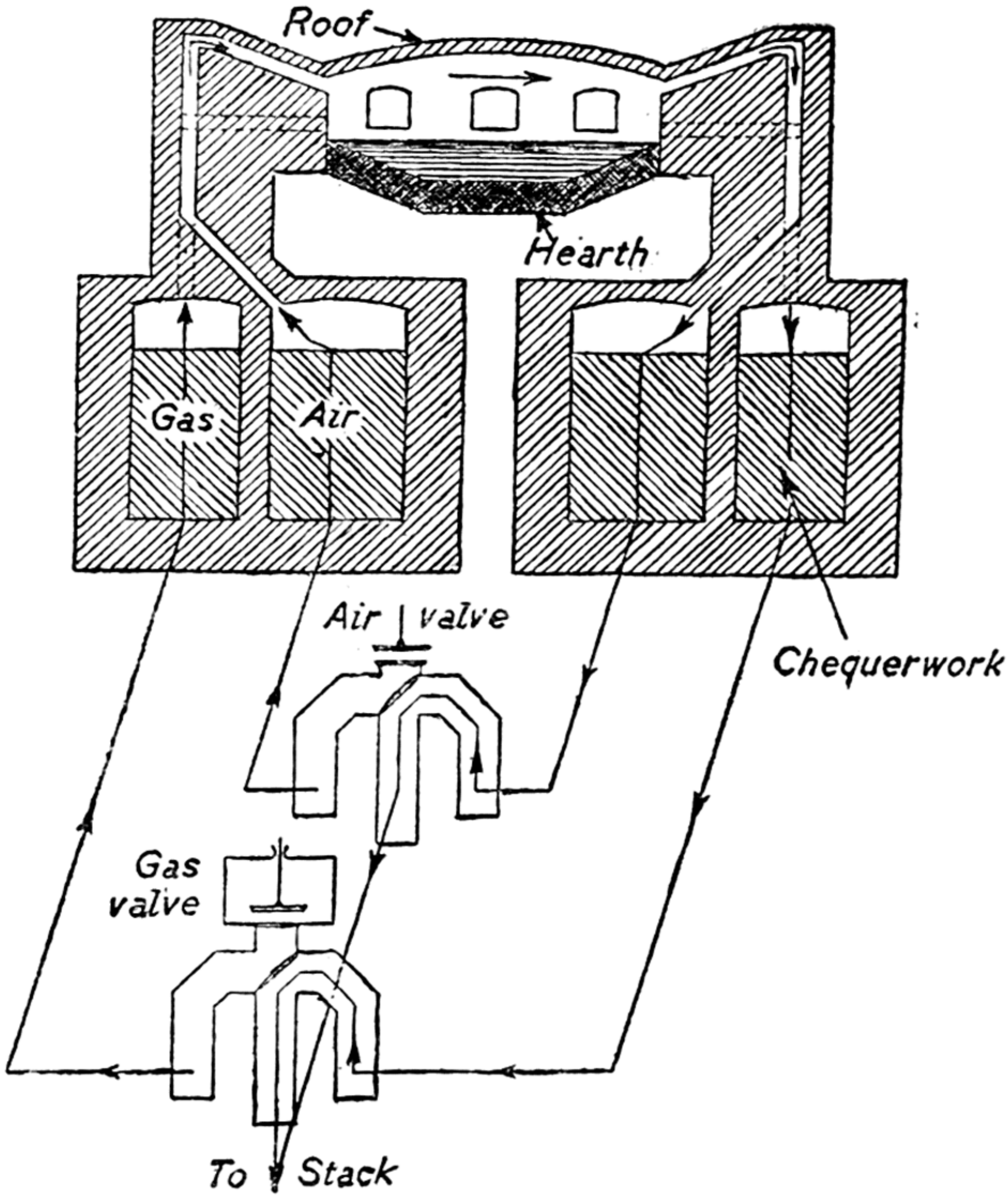


FIG. 251. General Arrangement of Open-hearth Plant

In arc furnaces the heat required is generated by an electric arc struck either between two carbon electrodes, or pairs of electrodes, or between carbon electrodes and the charge. The latter modification, known as a "direct-arc furnace," is of greater importance in steel-making. Such furnaces are usually lined with basic refractory material and generally work with a charge composed of steel scrap—in fact, steelmaking by this process is essentially steel refining and is normally only employed for the manufacture of high-grade alloy steels, such as are employed in increasingly large quantities by the aeronautical, automobile, machine tool and other industries.

High-frequency induction furnaces are essentially melting furnaces for the production of highly-alloyed steels from virgin materials.

Types of Steels. All commercial steels contain varying amounts of carbon, manganese, silicon, sulphur and phosphorus, and often in addition, such elements as nickel, chromium, molybdenum and vanadium. In carbon steels the only elements present are carbon, manganese up to about 1 per cent, silicon up to about 0·3 per cent, sulphur and phosphorus. An alloy steel may be said to be a steel which contains, in addition to carbon, sulphur and phosphorus, more than 1 per cent of manganese, or more than 0·3 per cent of silicon, or some other element or elements such as nickel, chromium, etc. In addition to classifying steels as either (*a*) carbon steels, and (*b*) alloy steels, it is often useful to distinguish between steels according to the uses to which they are applied. Thus a distinction may be made between (i) structural steels, and (ii) special purpose steels, this mode of classification is enlarged upon below.

TABLE 112

Classification of Steels

(i) Structural steels	(*a*) Carbon (*b*) Alloy
(ii) Special purpose steels	
Tool and die steels	(*a*) Carbon (*b*) Alloy (e.g. High-speed steel)
Stainless steels	(*a*) Martensitic (e.g. 14 per cent Cr:0·3 per cent C) (*b*) Austenitic (e.g. 18 per cent Cr:8 per cent Ni : 0·1 C)
Heat-resisting steels	
Steels employed for magnetic purposes	(e.g. Tungsten steels and cobalt steels)

Some typical analyses of various types of steels are given in Table 113 shown on p. 834.

Physical Properties of Iron

(*a*) Iron is a white metal.

(*b*) It is a heavy metal, density = 7·87.

(*c*) In the pure state it is soft, malleable and ductile, its mechanical properties being unaffected by quenching.

(*d*) Iron is highly magnetic, but when heated to temperatures of 770°C or above it ceases to be magnetic. On cooling below 770°C (the Curie point for iron) its magnetic characteristics return.

(*e*) Iron has a high melting point (1537°C).

(*f*) Iron is a polymorphic metal, three polymorphic forms being

recognized, known as α-, γ- and δ-iron respectively. The first-named, α-iron exists up to a temperature of 910°C and exhibits a body-centred cubic structure; γ-iron exists between 910°C and 1400°C, this polymorph exhibiting a face-centred cubic structure; δ-iron exists from 1400°C to the melting point of the metal, and has, like α-iron, a body-centred cubic structure.

TABLE 113

Typical Analyses of Various Types of Steels

Type of Steel	Chemical Composition (percentage) (Balance iron in each case)									
	C	Si	Mn	Ni	Cr	V	Mo	W	S	P
Mild steel . . .	0·15	0·20	0·50						0·05	0·05
Medium carbon steel .	0·40	0·15	0·60						0·03	0·04
High carbon steel . .	0·70	0·15	0·40						0·03	0·03
Tool steel . . .	1·20	0·15	0·25						0·02	0·02
3 per cent nickel steel .	0·30	0·30	0·60	3·00					0·02	0·02
Nickel-chromium-molybdenum steel . .	0·30	0·30	0·60	3·50	0·75		0·60		0·02	0·02
High-speed steel . .	0·80	0·30	0·35		4·50	1·50		18·0	0·02	0·02
Martensitic stainless steel	0·30				12·00				0·02	0·02
Austenitic stainless steel .	0·10			8·00	18·00				0·02	0·02
Heat-resisting steel . .	1·00	1·00		70·00	20·00			4·0		
Alnico (a magnet "steel")				20·00	10·00 per cent Co 10·00 per cent Al					

Chemical Properties of Iron

(*a*) Iron is stable in dry air at atmospheric temperature, but if heated it burns forming ferroso-ferric oxide, Fe_3O_4.

(*b*) When heated in steam, iron is also converted to ferroso-ferric oxide—

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2 \uparrow$$

(*c*) In moist air iron is said to "rust." The process of rust formation is very complex; it would appear that the presence of oxygen and water are essential, the presence of carbon dioxide and/or metallic salts accelerating rusting, whilst the presence of alkalis impedes it. Essentially the rusting of iron is an electrolytic process. Since all ordinary forms of commercial iron lack a uniformity of surface, when immersed in water those areas with lowest electrode potentials (*see* p. 268) function as anodes, the other portions of the iron surface serving as cathodes. The net result is that

moist iron functions as a short-circuited cell in which the following electrochemical reactions take place.

	At the Anode	At the Cathode
Reaction taking place .	Fe (metal) − 2 electrons = Fe^{++}	$2H_2O = 2H^+ + 2OH'$ $2H^+ + 2$ electrons $= H_2$
Net result . . .	Iron dissolves	Hydrogen is evolved

If no oxygen is present in the cell, the hydrogen evolved at the cathode polarizes the cell; in the presence of oxygen the hydrogen is oxidized to water and the iron passes continuously into the ionic state at the anode. The Fe^{++} and OH' ions react to form ferrous hydroxide, $Fe(OH)_2$ which, in turn reacts with carbon dioxide to yield ferrous carbonate, $FeCO_3$. The ferrous carbonate is then oxidized by the oxygen of the air to basic ferric carbonate, $Fe(OH)_2(HCO_3)$ or to $Fe(OH)(HCO_3)_2$, or both, which are then hydrolyzed to ferric hydroxide, $Fe(OH)_3$; and the ferric hydroxide is more or less dehydrated forming ferric oxide, $Fe_2O_3 . xH_2O$. Since ferric oxide is more or less hygroscopic, rusting accelerates with the passage of time since ferric oxide tends to maintain the iron surface in a moist condition.

(*d*) Iron is readily attacked by dilute sulphuric and hydrochloric acids forming the corresponding ferrous salts and evolving hydrogen.

With nitric acid, different products result according to the concentration of the acid. Thus dilute nitric acid (specific gravity below 1·034) yields ferrous nitrate and sometimes ammonium nitrate; as the concentration of the acid increases, ferrous nitrate and ferric nitrate are successively the chief products. Concentrated nitric acid *passivates* the surface of iron rendering it inactive to many reagents; this passivity is due to the formation of an oxide film, actually ferroso-ferric oxide, Fe_3O_4. This passivity may be destroyed by scratching the iron surface.

(*e*) Iron combines directly with the halogens, sulphur and phosphorus.

(*f*) With carbon, iron forms iron carbide, Fe_3C (cementite). This compound is of considerable importance since it is because of the varying solid solubility of Fe_3C in α-ion and γ-iron that steels are capable of hardening when heated to red heat and then quenched (or immersed) in water. Iron carbide will only dissolve to the extent of 0·03 per cent in α-iron—and this is at 723°C; at room temperature the solid solubility is in the region of 0·006 per cent. In γ-iron, however, Fe_3C exhibits a higher solubility of 1·7 per cent (at 1130°C). Thus, on quenching a steel—which at red heat is a solid solution of Fe_3C in γ-iron—a supersaturated

solid solution of Fe_3C in α-iron is produced in which there exists a considerable degree of internal strain. The result is that such quenched steel exhibits a pronounced hardness—in fact, it is commonplace to state that such material is "glass hard," by which is implied that its hardness is so great that it will scratch glass.

Compounds of Iron

Iron forms two series of compounds, those in which a valency of two is exhibited—the ferrous compounds; and those in which a valency of three is exhibited—the ferric compounds.

Ferrous Oxide, FeO, is a black powder produced either by the reduction of ferric oxide with hydrogen at 300°C, or alternatively by heating ferrous oxalate—

$$FeC_2O_4 . 3H_2O = FeO + CO\uparrow + CO_2\uparrow + 3H_2O$$

On exposure to the atmosphere it readily undergoes oxidation, in certain cases spontaneous combustion occurring, ferric oxide being produced. Ferrous oxide is a basic oxide readily reacting with dilute acids to form the corresponding ferrous salts.

Ferrous Hydroxide, $Fe(OH)_2$, is obtained as a white precipitate when a solution of an alkali hydroxide or ammonium hydroxide is added to the solution of a ferrous salt; the presence of air dissolved in the reagents causes the precipitate usually to assume a greenish colour. Ferrous hydroxide is readily oxidized in solution to ferric hydroxide—

$$4Fe(OH)_2 + \underset{\text{from the air}}{O_2} + 2H_2O = 4Fe(OH)_3$$

Ferrous hydroxide is a stronger base than ferric hydroxide as is indicated by the fact that it will form a *carbonate*, a *bicarbonate* and a very stable *sulphide*. Ferrous hydroxide unlike ferric hydroxide is soluble in ammonium chloride; it is therefore necessary in the Group Separation of the metals in qualitative analysis to ensure that any iron present is oxidized to the ferric state prior to the addition of ammonium chloride and ammonium hydroxide —the group reagents for Group 3 of the usual qualitative analytical scheme. This oxidation is usually carried out by boiling the solution, after the separation of Group 2, with a few drops of concentrated nitric acid.

Ferric Oxide, Fe_2O_3. This oxide occurs in nature as red hæmatite (kidney iron ore, or specular iron ore). It is also known as an article of commerce under such names as *jeweller's rouge*, *Venetian red*, *crocus powder*, *crocus martis* and *colcothar*. In the laboratory ferric oxide may be prepared by heating ferrous sulphate—

$$2FeSO_4 = Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

Alternatively, it may be prepared by heating ferric hydroxide. Ferric

oxide reacts with acids to form the corresponding ferric salts. Apart from the use of ferric oxide (as red hæmatite) as a source of metallic iron, it is employed in industry as an abrasive (jeweller's rouge, crocus powder, etc.), and as a red pigment (red ochre and Venetian red). A naturally-occurring hæmatite known as *micaceous hæmatite* is black in colour and finds application as a black pigment and for the making of welding rod coatings.

Ferric Hydroxide, $Fe(OH)_3$, is precipitated when a solution of a caustic alkali or ammonium hydroxide is added to the solution of a ferric salt. Ferric hydroxide is dark brown in colour; unlike aluminium hydroxide it is insoluble in excess alkali. On allowing the precipitate to dry, or on heating, ferric hydroxide suffers dehydration, ferric oxide being formed. Ferric hydroxide is a very weak base, it reacts with acids forming the corresponding ferric salts which in aqueous solution are hydrolyzed.

Ferroso-ferric Oxide, Fe_3O_4 (*Magnetite*, *lodestone*) is the most stable oxide of iron. It is formed when iron is heated in air or in oxygen. This oxide is probably an example of a "compound" oxide—being analogous to Pb_3O_4 and Mn_3O_4 in this respect. On treatment with acids it yields solutions containing a mixture of the corresponding ferrous and ferric salts.

Salts of Iron

Ferrous Carbonate, $FeCO_3$, is produced as a white precipitate when air-free solutions of sodium carbonate and a ferrous salt are mixed. Contact with the air leads to oxidation of the ferrous carbonate which first becomes green and finally red owing to the production of ferric hydroxide by hydrolysis. Ferrous carbonate dissolves readily in water containing dissolved carbon dioxide owing to the formation of soluble *ferrous bicarbonate*, $Fe(HCO_3)_2$, a salt only known in solution.

$$FeCO_3 + CO_2 + H_2O \rightleftharpoons Fe^{++} + 2(HCO_3)'$$

Ferrous Sulphate, $FeSO_4$, (*Green vitriol* or *copperas*) is prepared in the laboratory by the action of dilute sulphuric acid on metallic iron, the salt being obtained in the form of the green heptahydrate by evaporation of the resulting solution. On a commercial scale, green vitriol is obtained by evaporation of the residues of pickling baths (originally containing sulphuric acid) used for the descaling of mild steel sheets prior to tinplating and galvanizing. When strongly heated, ferrous sulphate is decomposed, ferric oxide, sulphur dioxide, sulphur trioxide and water being formed, thus—

$$FeSO_4 . 7H_2O \rightarrow FeSO_4 . H_2O \xrightarrow{300°C} FeSO_4$$

$$2FeSO_4 = Fe_2O_3 + SO_2 \uparrow + SO_3 \uparrow$$

Aqueous solutions of ferrous sulphates are capable of absorbing nitric

oxide and this property is utilized in the "brown-ring" test for nitrates (*see* p. 652). Ferrous sulphate forms a double salt with ammonium sulphate known as *ferrous ammonium sulphate* $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$. This double salt, sometimes known as *Mohr's salt* is less soluble in water than ferrous sulphate, and therefore is more readily obtained in a higher degree of purity; in addition, in solution Mohr's salt is less readily oxidized by the air. In the laboratory Mohr's salt is usually employed for the making up of "standard iron solutions." In commerce ferrous sulphate is employed for the manufacture of weed killers and for writing ink.

Ferrous Sulphide, FeS, is made by heating a mixture of iron filings and sulphur; it is also produced as a precipitate when aqueous solutions of ferrous salts are treated with an excess of an alkaline sulphide. Ferrous sulphide is easily melted and is usually cast into sticks or rods, which are black in colour. Ferrous sulphide in this form is used in the laboratory in the Kipp's apparatus (*see* p. 362) for the production of hydrogen sulphide.

Ferric Chloride, $FeCl_3$, is produced in the form of a sublimate of black scales when chlorine is passed over iron maintained at red-heat. This reaction is exothermic in nature. Ferric chloride melts at 300°C, its vapour at 450°C corresponding to the formula Fe_2Cl_6; at higher temperatures (i.e. up to about 750°C) the vapour density diminishes progressively to a value corresponding with the formula, $FeCl_3$. At temperatures in excess of 750°C, a further reduction in the value of the vapour density occurs, probably due to the dissociation of ferric chloride into ferrous chloride and chlorine—

$$2FeCl_3 \rightleftharpoons 2FeCl_2 + Cl_2 \uparrow$$

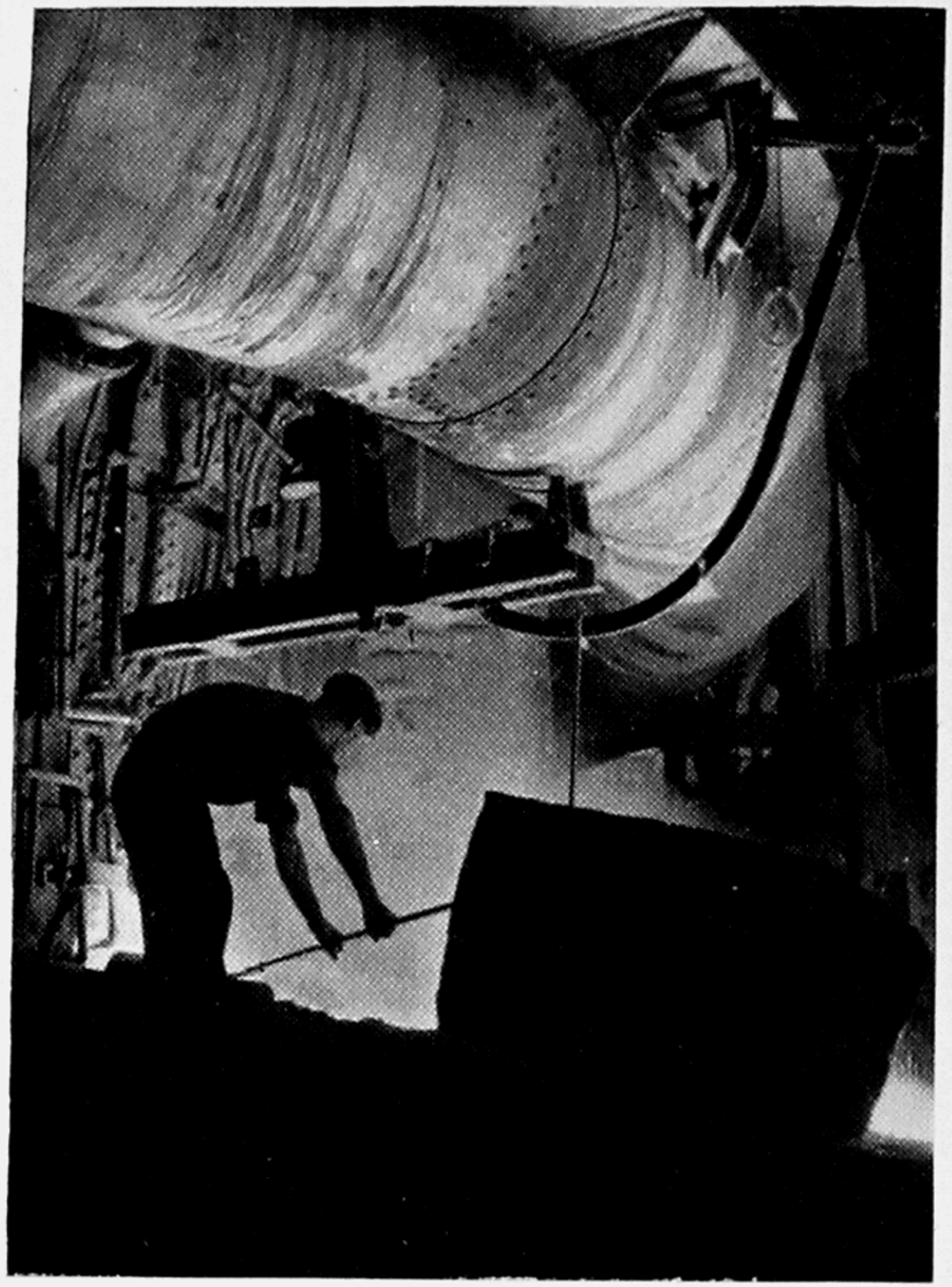
Ferric chloride may be obtained in the hydrated state by the action of hydrochloric acid (to which a little nitric acid has been added) on metallic iron, ferrous carbonate, or ferric oxide; by allowing the resulting solution to crystallize the hexahydrate, $FeCl_3 . 6H_2O$ is formed. Ferric chloride is very soluble in water, a whole series of hydrates being formed; such solutions are yellow in colour like the hydrate. Aqueous solutions hydrolyze, ferric hydroxide being precipitated; in certain cases the ferric hydroxide is retained as a colloidal suspension. On heating ferric chloride, ferric oxide is formed and hydrogen chloride and water liberated, thus—

$$2FeCl_3 . 6H_2O = Fe_2O_3 + 6HCl \uparrow + 3H_2O$$

Anhydrous ferric chloride is extremely deliquescent.

Ferric Sulphate, $Fe_2(SO_4)_3$, is obtained by heating ferrous sulphate with concentrated sulphuric acid—

$$2(FeSO_4 . 7H_2O) + 2H_2SO_4 = Fe_2(SO_4)_3 + SO_2 \uparrow + 16H_2O$$



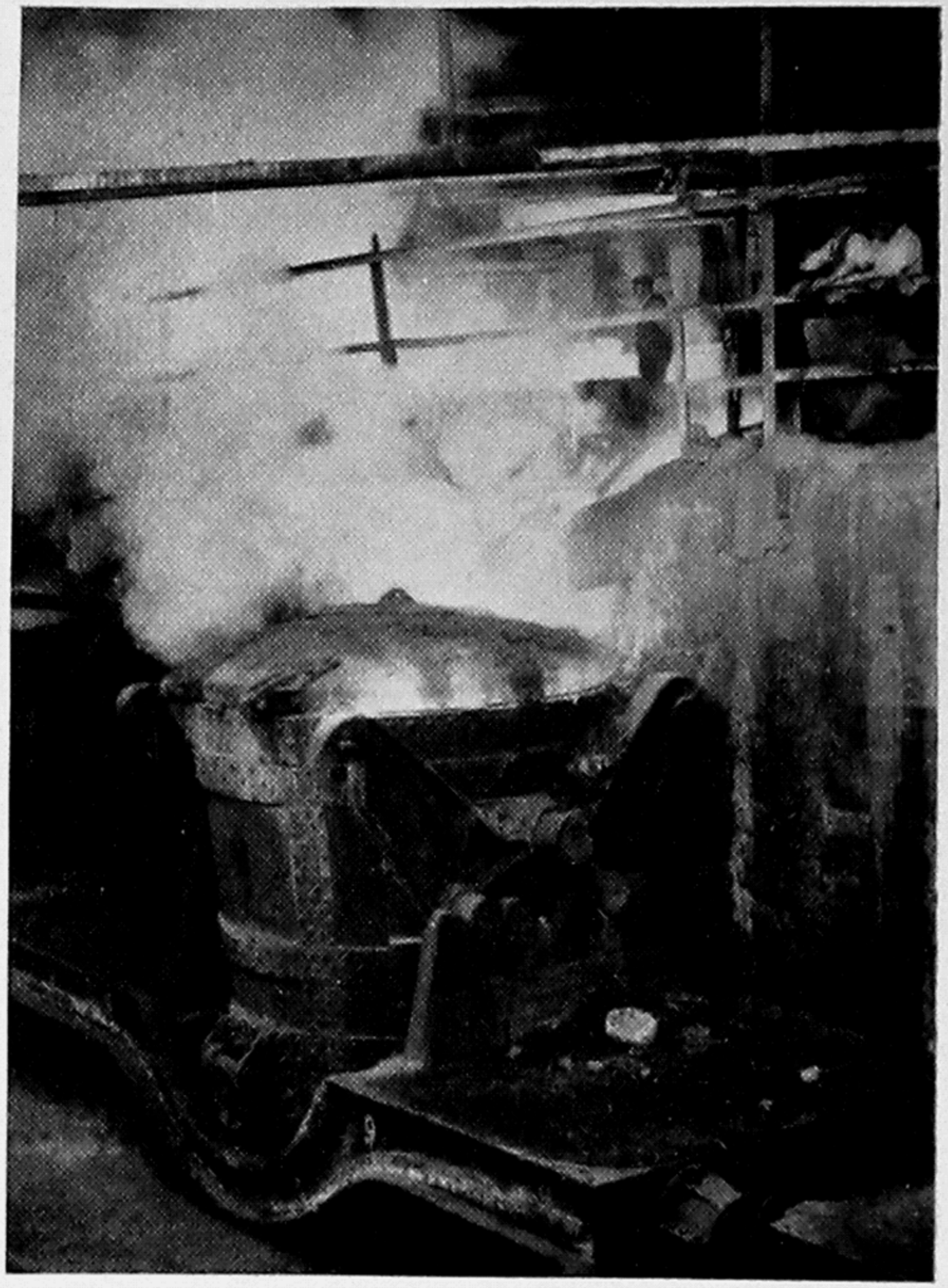
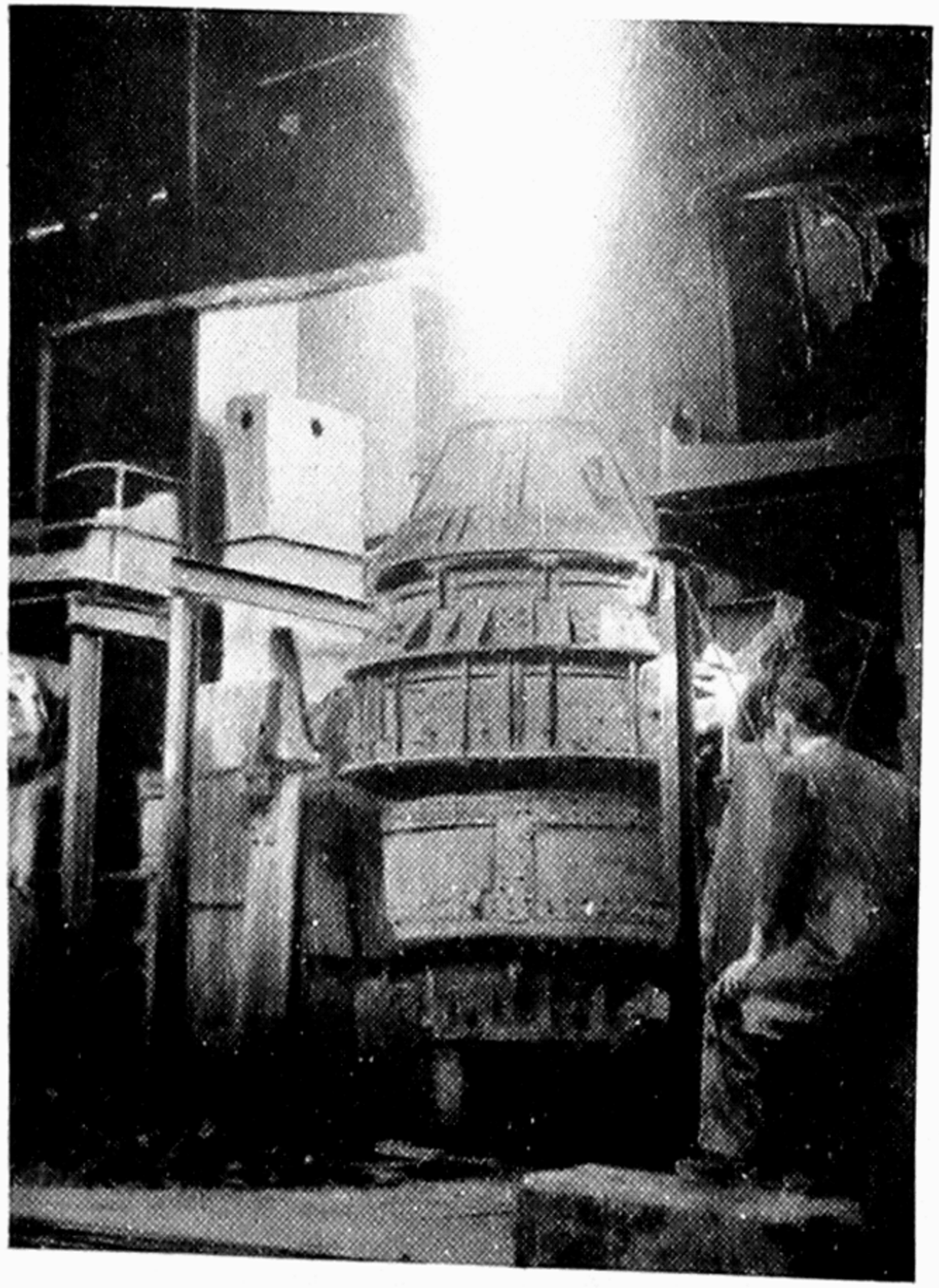


PLATE V

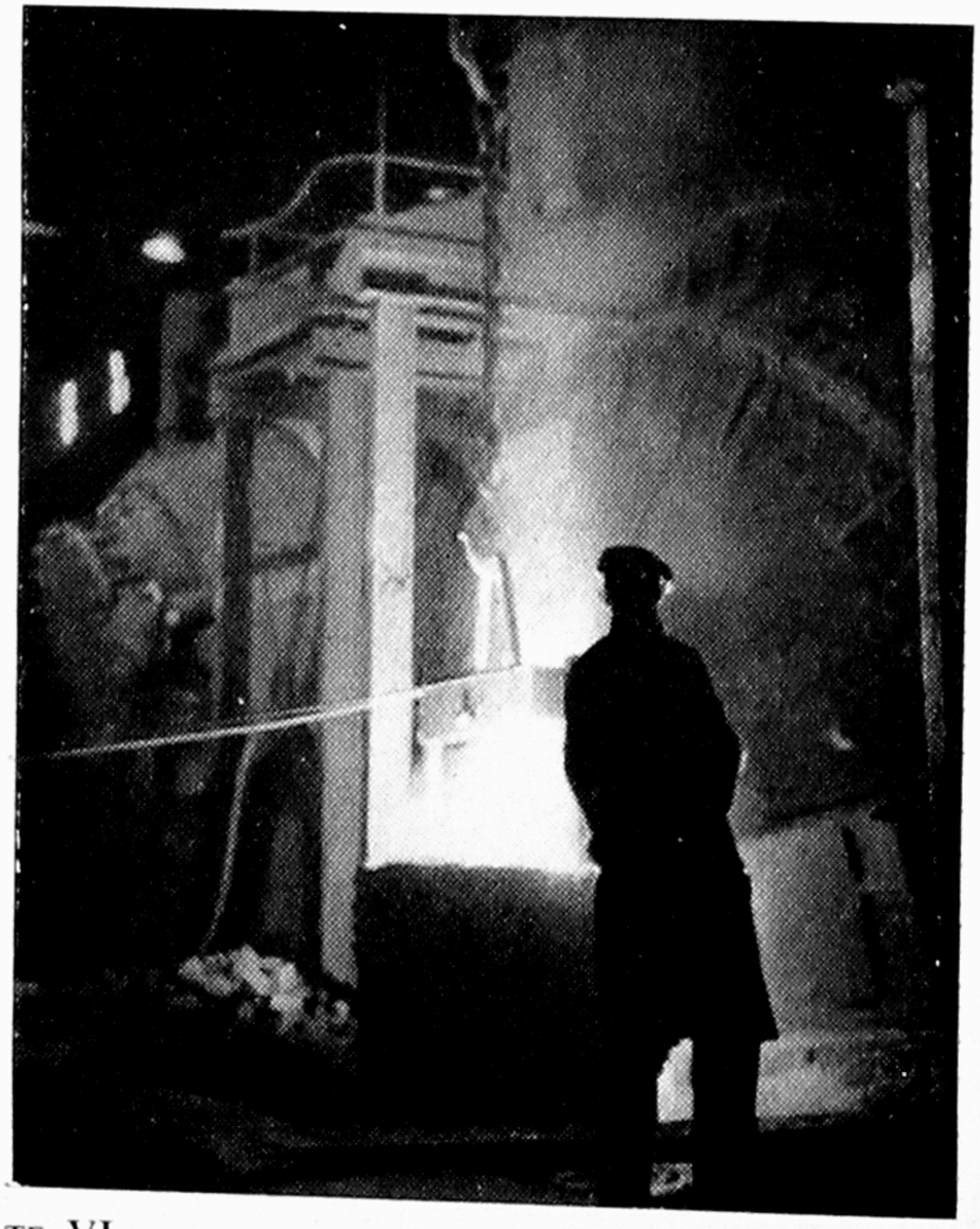
Production of Pig Iron: Corby, Northants

(*Left*) Tapping the Blast Furnace: the Iron is Tapped Four Times a Day

(*Right*) Molten Iron Runs out of the Blast Furnace into a Ladle which will be moved into the Converter House



(*a*) Bessemer Converter in Blow



(*b*) Teeming Steel from Bessemer Converter into Ladle

PLATE VI

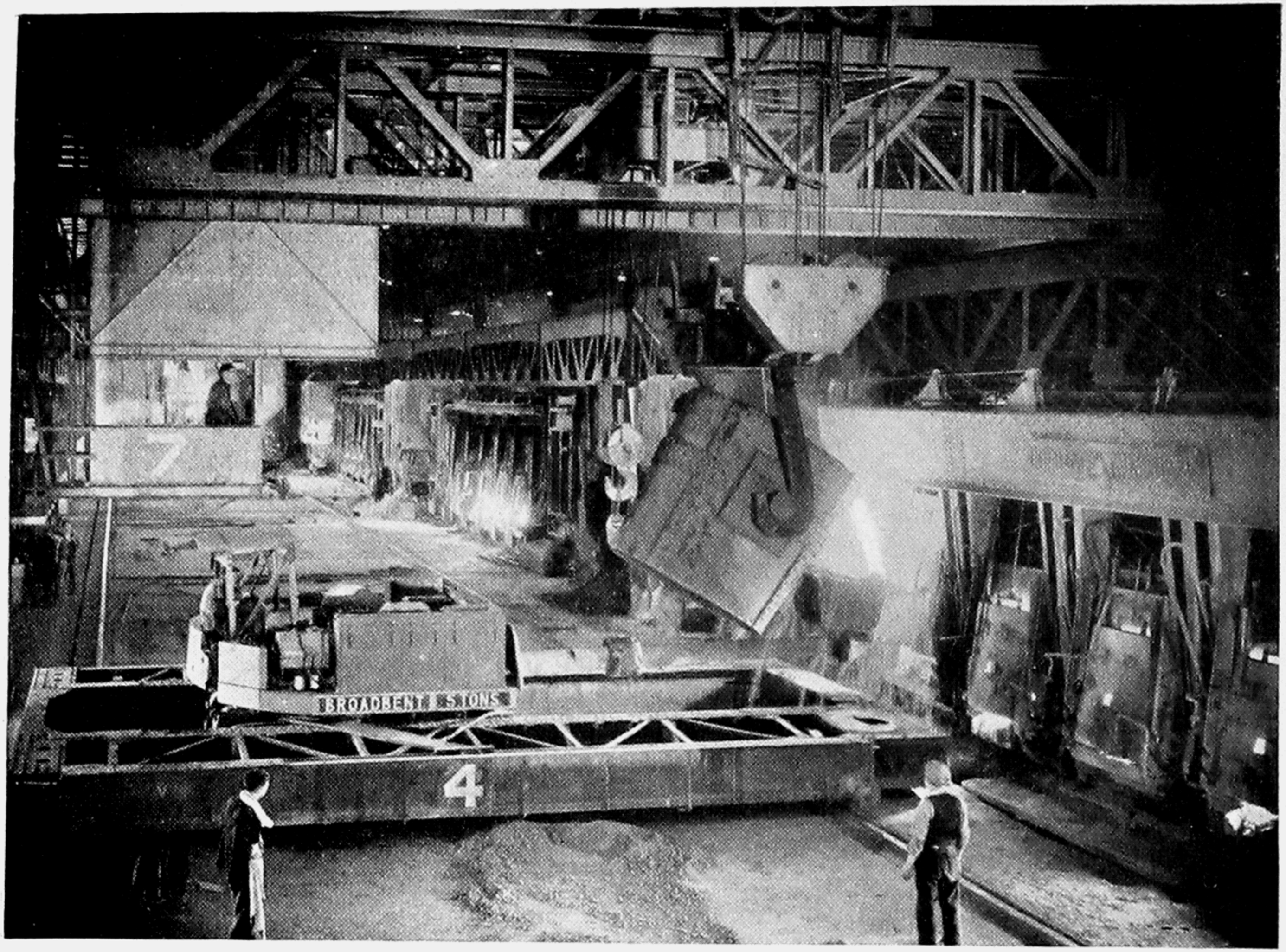


PLATE VII

Open Hearth Furnace—Charging with Molten Pig Iron

(Courtesy of Thomas Broadbent and Sons, Ltd., Huddersfield)

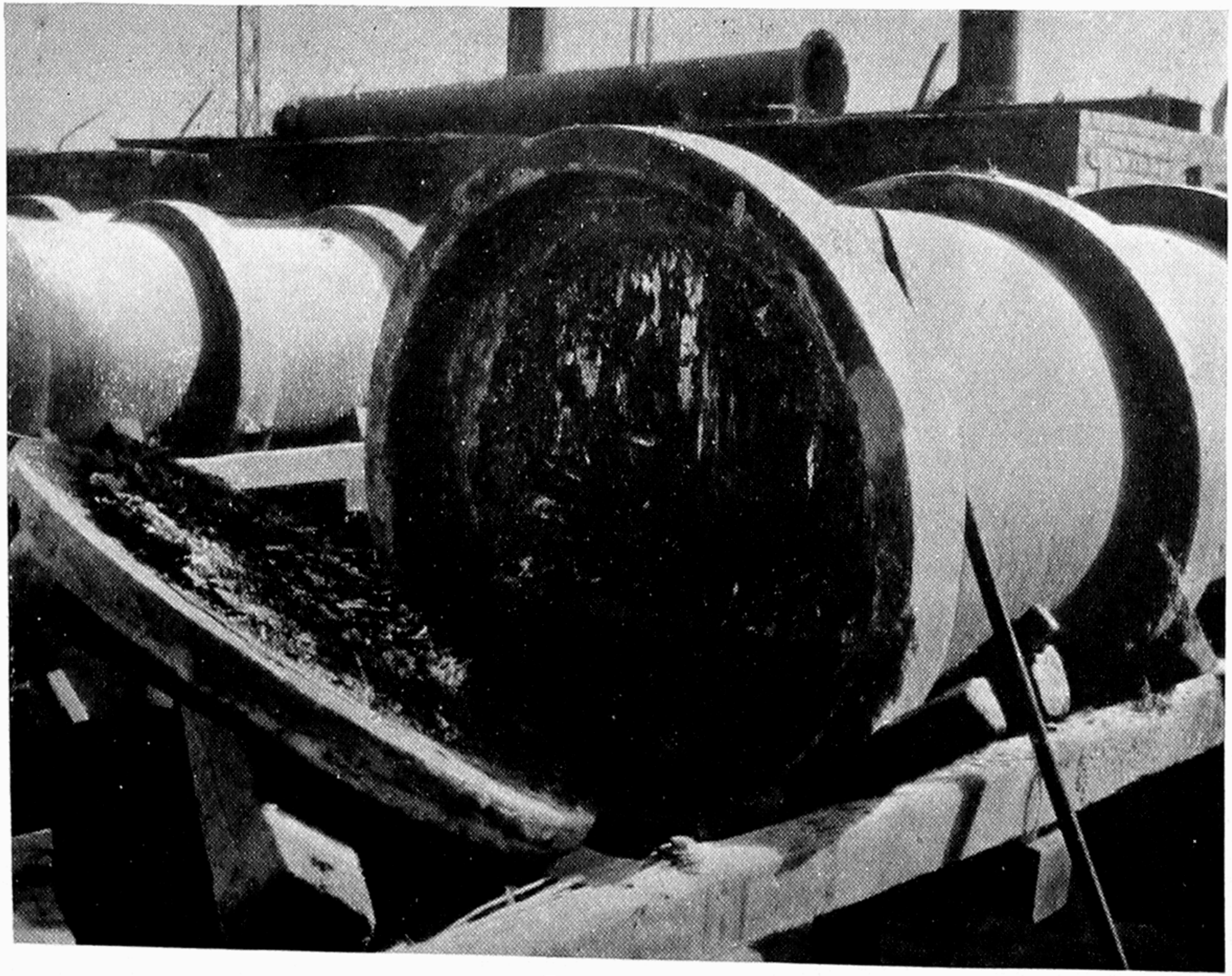


PLATE VIII

Iodine from Chilean Nitrate Mother Liquor

(*Courtesy of Chilean Nitrate Agricultural Service, London*)

When ferric sulphate is heated strongly it decomposes yielding ferric oxide and sulphur trioxide, not the oxide, sulphur dioxide and oxygen as produced when aluminium sulphate is heated.

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3 \uparrow$$

Ferric sulphate forms alums with the sulphates of the alkali metals, the most important being *ferric alum*, $Fe_2(SO_4)_3 . (NH_4)_2SO_4 . 24H_2O$. Ferric alum is employed in the laboratory for the purpose of preparing standard solutions of the ferric ion since it is practically the only ferric salt capable of purification by crystallization. It is pale violet in colour.

Cyanogen Compounds of Iron

Potassium Ferrocyanide, $K_4[Fe(CN)_6]$ (Yellow Prussiate of Potash). This compound is prepared in two ways—

(*a*) *From nitrogenous refuse*. Nitrogenous animal waste (such as horns, hoofs and hides) is heated with potassium carbonate and scrap iron; the potassium ferrocyanide is extracted with water. This method is now largely obsolete.

(*b*) *From spent oxide*. A large proportion of the volatile nitrogen in coal is liberated during coal gas manufacture, as hydrogen cyanide, HCN. This reacts with the oxide in the oxide purifiers to form ferrous and ferric cyanides, $Fe(CN)_2$ and $Fe(CN)_3$. These, in turn react with one another to form ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$ or Prussian blue.

The "spent oxide" containing this complex ferrocyanide is boiled with lime, soluble calcium ferrocyanide being leached from the residual mass. This calcium ferrocyanide is converted into the corresponding sodium or potassium salts by treatment with either sodium carbonate or with potassium carbonate.

Potassium ferrocyanide is one of the most stable of complex salts, in aqueous solution dissociation occurs thus—

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]''''$$

When heated with *dilute* sulphuric acid *hydrogen cyanide* is evolved—

$$2K_4[Fe(CN)_6] + 3H_2SO_4 = 3K_2SO_4 + K_2Fe[Fe(CN)_6] + 6HCN \uparrow$$

potassium ferrous ferrocyanide

If heated with *concentrated* sulphuric acid, *carbon monoxide* is liberated—

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO \uparrow$$

With ferrous salts, potassium ferrocyanide gives a precipitate of white *potassium ferrous ferrocyanide* $K_2Fe[Fe(CN)_6]$ which rapidly turns blue owing to oxidation to *potassium ferric ferrocyanide* $KFe[Fe(CN)_6]$. With

a ferric salt a precipitate of potassium ferric ferrocyanide is obtained direct; this deep blue coloured compound is known as *Prussian Blue*. A similar compound is obtained when solutions of sodium or ammonium ferrocyanide are added to a solution of a ferric salt. Thus, the general formula for Prussian blue may be written as $RFe[Fe(CN)_6]$, where R = K, Na or NH_4.

Potassium Ferricyanide, $K_3[Fe(CN)_6]$ (*Red Prussiate of Potash*). Potassium ferricyanide is obtained by the action of chlorine upon potassium ferrocyanide—

$$2K_4[Fe(CN)_6] + Cl_2 = 2KCl + 2K_3[Fe(CN)_6]$$

Potassium ferricyanide occurs as a red coloured crystalline substance containing three molecules of water of crystallization.

It is less stable than the corresponding ferrocyanide, and therefore functions as a mild oxidizing agent in alkaline solutions. It is somewhat unstable in light, forming the ferrocyanide; it is therefore usual to wash crystals of the ferricyanide with water in order to remove the coating of ferrocyanide when it is desired to prepare a solution of potassium ferricyanide.

Potassium ferricyanide reacts with ferrous ions to give a dark blue precipitate known as *Turnbull's blue*; its constitution is $KFe[Fe(Cn)_6]$ and this appears to be similar, if not identical, with Prussian blue. With ferric salts, potassium ferricyanide gives no precipitate in neutral solutions but the solution is usually coloured green or blue.

NICKEL

Occurrence. More than 85 per cent of the world's supply of nickel is obtained from the nickeliferous pyrrhotite deposits mined in the Sudbury district of Ontario, Canada. In these deposits the nickel is frequently present as the mineral *pentlandite*, (Ni,Fe)S; the nickel content of these ores rarely exceeds 5 per cent, in fact a content of 1–2 per cent nickel is very common. In association with the nickel there is copper present to an extent of approximately 2·5 per cent. These ores also yield platinum and the platinum metals as by-products.

Similar deposits to those of Sudbury, but not so extensive, occur near Petsamo in Finland. Nickel ores are also mined in New Caledonia in the South Pacific, these deposits are composed of a complex hydrated nickeliferous magnesium silicate known as *garnierite*.

Extraction. Only the extraction of nickel from the Sudbury deposits will be described here.

The ore is first crushed and then concentrated by the froth-flotation process. This concentrate is fed into multiple-deck roasters in which much of the sulphur is removed. The roasted material at a temperature just below its melting point is fed into reverberatory furnaces where it is

smelted with a flux; here more sulphur is removed and a matte produced consisting of the sulphides of nickel, copper and iron along with the precious metals and some lead. This matte is then blown in basic-lined Bessemer converters where more sulphur is burned off and the iron present in the matte oxidized to ferrous oxide which is slagged off as silicate slag by the aid of silica sand as a flux; this Bessemer matte contains about 46 per cent nickel, 35 per cent copper, 15 per cent sulphur and 0·8 per cent iron, along with the precious metals. If the precious metal content is low the Bessemer matte is often converted into the copper-nickel alloy known as Monel metal.

A large proportion of the matte rich in the precious metals is refined by the Mond process at Clydach, South Wales and with the object of reducing freight and handling costs it is usual to subject the Bessemer matte to a further refining process—the Orford process—before shipping to South Wales for refining by the Mond process. The Orford process depends principally upon the fact that copper sulphide combines with alkali metal sulphides on heating to form a double sulphide, whereas nickel sulphide remains unaffected. Thus, the Bessemer matte is heated in a cupola with nitre cake (sodium sulphate) and coke when the double sulphide of copper and sodium is formed and the nickel sulphide left unaffected. When this product is tapped into large pots the material separates into two layers, the lighter, upper layer, called "tops" of the double sulphide of copper and sodium, whilst the lower layer, called "bottoms" is of nickel sulphide. The separation of nickel and copper is still incomplete after one fusion so the process is repeated when a second "bottoms" with about 1·5 per cent copper and 72 per cent nickel results; this last product, "second bottoms" is then calcined to remove a portion of the sulphur and is then shipped to Clydach, South Wales for treatment by the Mond process.

In the Mond process the product from the Orford process is ground and then calcined to reduce the sulphur content still further and the solid residue treated in reduction towers where it meets an upward stream of water gas at a temperature of about 350°C. The reduced nickel thus obtained is next treated with producer gas rich in carbon monoxide, at a temperature of 50°–60°C, whereby the nickel is converted into the volatile *nickel carbonyl*, $Ni(CO)_4$, which passes out of the volatilizer mixed with producer gas. This gaseous mixture is then led into decomposing towers which are heated internally to a temperature of approximately 180°C, at which nickel carbonyl suffers decomposition into metallic nickel and carbon monoxide.

$$Ni + 4CO \rightleftharpoons^{50°-60°C}_{180°C} Ni(CO)_4$$

The nickel is deposited from the decomposing nickel carbonyl upon nickel shot. When the nickel shot have increased sufficiently in size the larger

ones are separated from the smaller particles by screening, the smaller particles being returned to the top of the decomposing tower to have more nickel deposited upon them. The nickel obtained by the Mond process has a purity of approximately 99·8 per cent.

The non-volatile residues from the volatilizers contains all the platinum metals, gold and silver along with small quantities of selenium and tellurium. This source provides the world's largest supply of the platinum metals.

Physical Properties of Nickel

(*a*) Nickel is a silvery-white metal, capable of taking a high polish.

(*b*) The metal is malleable, ductile and hard.

(*c*) Nickel, like iron, can be magnetized although not to the same degree. It has a magnetic transformation point at approximately 320°C.

(*d*) Nickel has a high melting point (1455°C).

(*e*) The metal has a high density, 8·69 in the cast state, and 8·87 for rolled metal.

Chemical Properties of Nickel

(*a*) Nickel tarnishes slowly in the air at atmospheric temperature, although when in a finely divided form it is readily oxidized, becoming red hot in the process; the product is nickelous oxide, NiO.

(*b*) Nickel is unaffected by water, but decomposes steam at red heat.

(*c*) Dilute hydrochloric acid and dilute sulphuric acid act only slowly upon nickel forming the chloride and sulphate respectively. Dilute nitric acid, however, readily attacks the metal, whilst concentrated nitric acid passivates nickel.

(*d*) Nickel is very resistant to attack by alkalis.

(*e*) Nickel (and its compounds) exhibit strong catalytic activity in many types of reactions, for example the hydrogenation of oils.

Uses of Nickel. Nickel is marketed in a variety of forms, these are (*a*) grains or powder reduced from nickel oxide at low temperature without fusion occurring; (*b*) nickel shot produced by the Mond process; (*c*) electrolytic nickel; (*d*) nickel blocks or shot produced by the reduction of nickel oxide above the melting-point of nickel and then granulating the nickel by pouring the metal into water; and (*e*) malleable nickel produced as detailed under (*d*) except that the material is treated with a deoxidizing agent such as magnesium.

Malleable nickel is fashioned into various forms such as sheet, rod and wire and used for the manufacture of such items of laboratory ware as tongs, crucibles, spatulas, etc., for the electrodes of radio valves, chemical plant, cooking utensils, dairy and food-handling equipment, pyrometer sheaths, and for the anodes of such batteries as the Edison type. Malleable nickel is also used for the production of coins. Nickel is employed in the electrodeposited form as an undercoat for chromium.

Finely-divided nickel is employed as a catalyst, in the hydrogenation or hardening of fats and oils used in the manufacture of soap and food products; for the manufacture of hydrogen from natural gas or waste gases from petroleum refining or cracking processes; for the removal of organic sulphur and carbon monoxide from town gas; and for the manufacture of acetic acid from acetylene, and methane from carbon monoxide and hydrogen.

Nickel is a constituent of many types of alloys, both ferrous and non-ferrous. In ferrous alloys nickel is used in the production of the high-strength nickel and the nickel-chromium steels containing 1–5 per cent nickel; the stainless steels contain nickel in contents varying from 8–25 per cent. An iron-nickel alloy containing approximately 35 per cent nickel is known as *Invar*; this alloy exhibits an extremely small coefficient of thermal expansion and therefore finds application for the manufacture of parts of surveying instruments, measuring instruments, pendulums for clocks, and certain components in accurate chronometers, etc. Nickel-clad steel is of fairly recent introduction and consists of steel sheathed with nickel; this composite material has all the advantages of high corrosion-resistant nickel but with the strength of steel.

Of the non-ferrous alloys one of the most important is *Monel metal*, an alloy containing approximately 70 per cent nickel and 30 per cent copper; this material exhibits a high resistance to corrosion along with high strength, high resistance to shock and good malleability and ductility. *Constantan* is another copper-nickel alloy (40 per cent Ni: 60 per cent Cu), this alloy is employed for the fabrication of thermocouples and electrical resistances. The nickel silvers are essentially copper-zinc alloys or brasses containing nickel in amounts varying from 10–25 per cent; these alloys are characterized by their whiteness and excellent resistance to corrosion; they form the basis of silver-plated tableware (E.P.N.S. electroplated nickel silver). Nickel forms an important alloy with chromium —80 per cent nickel and 20 per cent chromium—known as *Nichrome*; this alloy is used extensively for the fabrication of electrical resistances. Nickel is often present in tin bronzes with the object of enhancing the resistance to corrosion, or of modifying the colour when these alloys are employed for architectural purposes.

Compounds of Nickel

Oxides and Hydroxides. Nickel forms two oxides, *nickelous oxide*, NiO and *nickelic oxide*, Ni_2O_3, and possibly other oxides exist. *Nickelous oxide* is formed by the ignition of the finely-divided metal in the air, or by heating the hydroxide or the carbonate; the anhydrous oxide is green in colour, but changes to a yellow colour when heated; it is a basic oxide which reacts with acids to form nickelous salts.

Nickelic Oxide, is a black oxide obtained by gently heating nickelous nitrate; the application of strong heating yields nickelous oxide.

Nickelous Hydroxide, $Ni(OH)_2$, is obtained as pale green precipitate when the aqueous solution of a nickelous salt is treated with an alkali. This hydroxide is insoluble in excess of sodium or potassium hydroxide solution but reacts with excess ammonium hydroxide, as also does copper hydroxide, to form a soluble blue complex, $[Ni(NH_3)_4](OH)_2$.

Salts. Nickel only forms one series of stable salts, the nickelous salts. These salts are formed when the metal or the hydroxide is dissolved in an acid. The hydrated salts are green in colour, and form green coloured solutions, but the anhydrous salts are in most cases yellow in colour. Many of the anhydrous salts are capable of absorbing ammonia to form violet coloured additive compounds.

Nickel Sulphate, as obtained by crystallization from aqueous solutions, has the composition $NiSO_4 . 7H_2O$; it occurs in the form of green coloured rhombic crystals which are isomorphous with the sulphates of zinc, iron and magnesium. The anhydrous salt is obtained when the hydrate is heated strongly. Nickel sulphate forms a green coloured double sulphate with ammonium sulphate, namely nickel ammonium sulphate $NiSO_4 . (NH_4)_2SO_4 . 6H_2O$ which is isomorphous with ferrous ammonium sulphate. Nickel nitrate is prepared by the action of dilute nitric acid upon metallic nickel, and on evaporation of the resulting solution green monoclinic crystals of the hexahydrate $(Ni(NO_3)_2 . 6H_2O$ separate out.

Hydrated Nickel Chloride is obtained in the form of green crystals of $NiCl_2 . 6H_2O$ on evaporating a solution of nickel or nickel oxide in hydrochloric acid. The *anhydrous chloride* is obtained either by dehydration of the hexahydrate in a stream of hydrogen chloride, or alternatively by the direct action of chlorine upon finely-divided nickel. The anhydrous chloride is a yellow solid.

Nickel Carbonate, $NiCO_3$, is obtained as a pale green precipitate when a solution of sodium bicarbonate is added to the aqueous solution of a nickelous salt; the addition of sodium carbonate yields a basic nickel carbonate.

Nickel Sulphide, NiS, is formed as a black precipitate when an alkaline sulphide is added to the aqueous solution of a nickelous salt. In the freshly precipitated form nickelous sulphide is soluble in acids, but on standing, or alternatively on boiling with water the precipitated sulphide is converted into an insoluble form which is insoluble in acids; in this respect nickel sulphide is similar to cobalt sulphide.

Nickelous Cyanide, $Ni(CN)_2$, is formed as a pale green precipitate when potassium cyanide solution is added to the aqueous solution of a nickelous salt, thus—

$$NiSO_4 + 2KCN = Ni(CN)_2 \downarrow + K_2SO_4$$

The addition of excess potassium cyanide solution results in the formation of soluble potassium nickelo-cyanide, as follows—

$$Ni(CN)_2 + 2KCN = K_2[Ni(CN)_4]$$

potassium nickelo-cyanide

A similar reaction occurs when excess potassium cyanide is added to an aqueous solution of a cobalt salt, potassium cobalto-cyanide, $K_4[Co(CN)_6]$ being formed. On boiling, or alternatively on addition of an oxidizing agent such as sodium hypochlorite or sodium hypobromite, potassium cobalto-cyanide is oxidized to potassium cobalti-cyanide, $K_3[Co(CN)_6]$, whereas on boiling or on the addition of an oxidizing agent to potassium nickelo-cyanide, a black precipitate of hydrated nickel dioxide, NiO_2 is obtained. These reactions are sometimes employed as a means of identifying nickel in the presence of cobalt.

COBALT

Occurrence. Practically the whole of the world's supply of cobalt is obtained as a by-product from complex ores which are mined primarily for the other metals (e.g. copper and silver) which they contain. In these complex ores, cobalt is present as sulphide, arsenide and sulpharsenide as the minerals *linnaeite*, Co_3S_4, *smaltite*, $CoAs_2$ and *cobaltite*, CoAsS. At present, the chief sources of cobalt are the cobalt-bearing copper ores in the Katanga district of Belgian Congo where the deposits carry 2–4 per cent cobalt, and Northern Rhodesia where the ores carry an average of about 0·5 per cent cobalt.

Extraction of Cobalt. Treatment of the ore in the blast furnace brings the cobalt into the slag which, after reduction in an electric furnace, forms an iron-copper-cobalt alloy containing about 40 per cent cobalt. This material is dissolved in hydrochloric acid and the cobalt precipitated as hydrated cobaltic oxide by means of bleaching powder. The oxide is collected, dried, and reduced by heating in a current of hydrogen.

$$Co_2O_3 + 3H_2 = 2Co + 3H_2O$$

A very pure form of the metal may be prepared by heating cobalt oxalate at high temperatures. Cobalt of the highest purity is prepared by the thermal decomposition of cobalt carbonyl, or by electrodeposition from a solution of cobaltous sulphate.

Physical Properties of Cobalt

(*a*) Cobalt is a brilliant, bluish-white metal.

(*b*) It exhibits a high melting point (1490°C) and a high boiling point (2900°C).

(*c*) It is a heavy metal, density 8·9.

(*d*) Cobalt is a polymorphic metal, being of a hexagonal close-packed

structure up to 420°C, and face-centred cubic from 420° up to the melting point.

(*e*) Cobalt is the most magnetic metal known after iron, retaining its magnetism up to 1115°C.

(*f*) It is a hard, strong metal, electrodeposited cobalt being considerably harder than the annealed material.

Chemical Properties of Cobalt

(*a*) Cobalt is stable in air at ordinary temperatures, but if heated it burns to cobalto-cobaltic oxide, Co_3O_4.

(*b*) At red heat it will decompose steam.

(*c*) When finely divided, it ignites spontaneously in an atmosphere of the oxides of nitrogen.

(*d*) At 470°C, cobalt reacts with ammonia to form cobalt nitride, Co_4N_2, which decomposes at 600°C.

(*e*) At a pressure of 100 atmospheres, finely divided cobalt reacts with carbon monoxide at a temperature of approximately 200°C, forming orange-red crystals of cobalt carbonyl, $Co_2(CO)_8$. In the formation of its carbonyl, cobalt differs from nickel in that nickel carbonyl is formed at atmospheric pressure and at a lower temperature.

(*f*) Cobalt reacts with the halogens to form the corresponding cobalt halides.

(*g*) Cobalt is attacked by dilute mineral acids, forming cobaltous salts. Concentrated nitric acid renders the metal passive owing to the formation of a skin of cobalto-cobaltic oxide.

(*h*) Cobalt is not attacked by alkalis.

Uses of Cobalt. Cobalt is chiefly employed in the production of alloys, its use in this connexion being chiefly due to the following characteristics—(*a*) the imparting of a high "red-hardness" (i.e. hardness at red heat), (*b*) increased wear resistance, and (*c*) the ability of cobalt to confer magnetic characteristics on the alloy.

Some of the chief alloys of cobalt are as follows.

The Stellites; cast carbides consisting of tungsten and chromium carbides set in a ground-mass of chromium and cobalt. These alloys are used for cutting tools and for use as valve seatings for aero engines.

Magnetic materials;

(*a*) Cobalt steel: 0·8 per cent C; 9 per cent Cr; 13 per cent Co; Balance = Fe.

(*b*) Alnico: 10 per cent Co; 20 per cent Ni; 10 per cent Al; Balance = Fe.

High-speed steels; 0·68–0·85 per cent C; 20 per cent W; 1·5–2 per cent V; 5–18 per cent Co; Balance = Fe.

Cobalt is co-deposited along with nickel in certain types of "bright" nickel electrodeposits.

Compounds of Cobalt

Oxides. There are three principal oxides of cobalt, analogous to the oxides of iron. *Cobaltous oxide*, CoO, is a greenish-grey powder formed by heating cobaltous hydroxide, carbonate or nitrate to a temperature of 1000°C, in the absence of air. It is stable in air at atmospheric temperature, but when heated to 600–700°C, it reacts with oxygen forming Co_3O_4. *Cobaltic oxide*, Co_2O_3, is produced when cobaltous nitrate or carbonate are heated in air—

$$4Co(NO_3)_2 = 2Co_2O_3 + 8NO_2 \uparrow + O_2 \uparrow$$

Cobaltic oxide is a brown powder which when heated between 373° and 700°C, is converted into a black powder, *cobalto-cobaltic oxide*, Co_3O_4.

Salts. Cobaltous and cobaltic oxides give rise to two series of cobalt salts, the cobaltous salts and cobaltic salts respectively. The latter however are only stable when they exist in the form of complex salts. Thus, solution of any of the three oxides in acids results in the formation of the corresponding cobaltous salt.

$$CoO + 2HCl = CoCl_2 + H_2O$$
$$Co_2O_3 + 6HCl = 2CoCl_2 + 3H_2O + Cl_2 \uparrow$$
$$Co_3O_4 + 8HCl = 3CoCl_2 + 4H_2O + Cl_2 \uparrow$$

The cobaltous salts are therefore the ordinary salts of cobalt; they are pink when hydrated or in solution, and blue when anhydrous.

Cobaltous Chloride, $CoCl_2$, is prepared in the anhydrous state by heating metallic cobalt in chlorine, and occurs in the form of blue scales. The hydrated salt, $CoCl_2 . 6H_2O$ is formed by the action of dilute hydrochloric acid on the metal, one of its oxides, carbonate or hydroxide. The hydrated salt is pink in colour and in solution, the solution probably containing the cation, $[Co . 6H_2O]^{++}$. The pink coloured solutions become blue in colour on adding hydrochloric acid, calcium chloride, or potassium chloride, whilst the addition of mercuric chloride or zinc chloride, or dilution with water causes the colour to change from blue to pink. This production of a blue colour has been attributed to the formation of the blue anion, $[CoCl_4]''$, and the production of a pink colour with mercuric chloride and a blue colour with calcium chloride is interpreted as indicating the readiness with which mercury forms a complex anion and calcium a cation, thus—

$$Co^{++}[HgCl_4]'' \qquad Ca^{++}[CoCl_4]''$$

Solutions of cobaltous chloride find application as so-called "invisible" ink, since the very pale pink colour of the solution is practically invisible whereas when the paper is dried (by warming) the anhydrous (blue) salt is formed which is clearly visible; on cooling to atmospheric temperature

the anhydrous salt reabsorbs moisture from the atmosphere and hence is converted into the hexahydrate again.

Cobaltous Nitrate, $Co(NO_3)_2$, is obtained in the form of the red hexahydrate by the action of nitric acid upon the metal, one of its oxides or the carbonate.

Cobaltous Sulphate, crystallizes with seven molecules of water of crystallization and is isomorphous with $FeSO_4 . 7H_2O$ and $NiSO_4 . 7H_2O$; it forms a double salt with ammonium sulphate, $CoSO_4 . (NH_4)_2SO_4 . 6H_2O$, which is analogous to ferrous ammonium sulphate.

Cobaltous Carbonate, $CoCO_3$, is obtained by the action of sodium bicarbonate solution saturated with carbon dioxide on the solution of a cobaltous salt. If this reaction is carried out at a temperature of approximately 140°C, the anhydrous carbonate results; at room temperature the hexahydrate is formed instead.

Although the simple cobaltic salts are unstable under normal conditions, there are a number of complex salts which are formed from the cobaltic ion. Thus, there are the *cobalt alums* of which one of the most important is the bright blue *ammonium cobalt alum*, $(NH_4)_2SO_4 . Co_2(SO_4)_3 . 24H_2O$ which is isomorphous with the other alums. In a similar manner the cobalti- and the cobalto-cyanides are comparable with the ferri- and the ferrocyanides. The addition of potassium cyanide solution to the solution of a cobaltous salt results in the formation of a precipitate of the pinkish-brown *cobaltous cyanide* which reacts with excess potassium cyanide to form a brown coloured solution containing the *cobaltocyanide ion*—

(*a*) $$Co^{++} + 2(CN)' = Co(CN)_2 \downarrow$$

(*b*) $$Co(CN)_2 + 4(CN)' = [Co(CN)_6]''''$$

Cobaltocyanides are readily oxidized, either by the halogens, or by boiling in air, to the cobalticyanides.

$$4K_4[Co(CN)_6] + 2H_2O + O_2 = 4K_3[Co(CN)_6] + 4KOH$$

from the air

The complex compounds, *sodium and potassium cobaltinitrites* are of importance in chemical analysis. If sodium nitrite is added to a solution of a cobaltous salt acidified with acetic acid there is formed sodium cobaltinitrate. The formula for this compound is $Na_3[Co(NO_2)_6$ and it is to be noted that it does not exhibit the usual reactions either for cobalt or for the nitrite radical; in fact it behaves as a sodium salt and reacts with aqueous solutions of potassium salts to form a yellow precipitate of potassium cobaltinitrite, $K_3[Co(NO_2)_6]$. Sodium cobaltinitrite therefore finds application in chemical analysis as a reagent for detecting the presence of potassium. These compounds are typical *co-ordination compounds*. Other examples of such compounds are the *cobaltammines* formed by the oxidation of solutions of cobaltous salts with excess ammonia.

PART III

ORGANIC CHEMISTRY

By

R. F. PHILLIPS, M.A., B.Sc. (Oxon), Ph.D. (Lond.), F.R.I.C.

CHAPTER 27

INTRODUCTION TO ORGANIC CHEMISTRY

THE term "Organic Chemistry" nowadays refers specifically to the chemistry of the compounds of carbon. These compounds may be of "organic" (or natural) origin in association with living matter, or they may be compounds which have been synthesized or otherwise prepared in the laboratory. If they contain carbon as an essential constituent of the molecule then they are classed as organic compounds.

This modern conception of organic chemistry is a very much broader one than was formerly understood by the term. It was for a long time accepted as an unalterable fact of nature that naturally-occurring compounds, of which sugar, fats, plant pigments, vegetable oils, may be quoted as examples, all owed their existence to their association with living matter. Some living or "vital" force was considered necessary for their formation, and so widely and generally accepted were these views that it was considered futile even to attempt to produce such substances by the usual chemical reactions of the laboratory. This "vitalistic theory" of organic chemistry however is now only of historical importance, although its effect in holding up for a considerable time the systematic investigation of the chemistry of these compounds should not be underestimated.

In 1828, Wohler inaugurated the modern conception of organic chemistry as the chemistry of the carbon compounds and opened the way for the enormous developments which have been made in the last century, by preparing in the laboratory a recognized organic compound, namely urea. On heating ammonium cyanate, a compound which may be prepared from inorganic materials, he succeeded in preparing and isolating urea, which is an excretion of certain animal organisms.

$$\underset{\text{ammonium cyanate}}{NH_4CNO} \rightarrow \underset{\text{urea}}{CO(NH_2)_2}$$

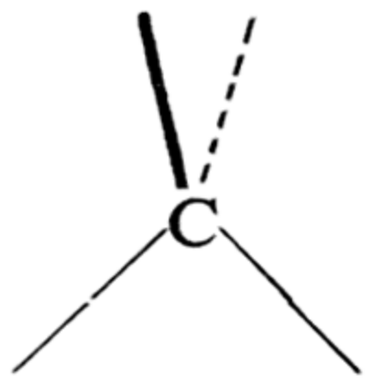
Nowadays, urea is made on a large scale (principally for use as an ingredient in the manufacture of certain plastics) by heating ammonia and carbon dioxide together under very high pressure. The synthesis of other organic compounds from purely inorganic materials soon followed and the way was opened for the study of organic compounds in the laboratory.

The distinction between organic chemistry and inorganic chemistry

as two more or less separate branches of chemistry is retained for the very good reason that the number of carbon compounds is so large as to be apparently unlimited. To-day, well over a quarter of a million compounds of carbon are known, and many more are being discovered and isolated every year. No other element can compare with carbon in this respect. So complex indeed is the field of organic chemistry that many chemists nowadays tend to specialize in its study and to call themselves "organic chemists."

The unique behaviour of carbon in forming such a large number of compounds may be traced to two particular properties—

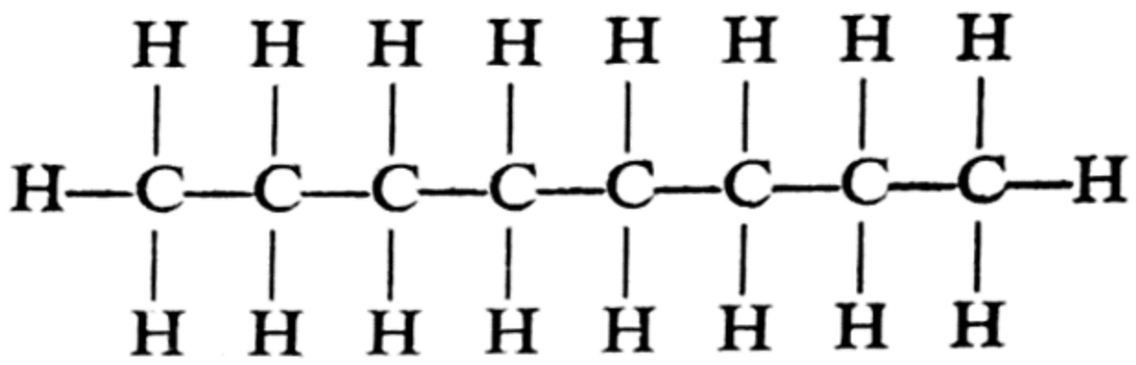
(*a*) The valency of carbon is four, the four valency bonds being covalent and having a spacial, tetrahedral arrangement—



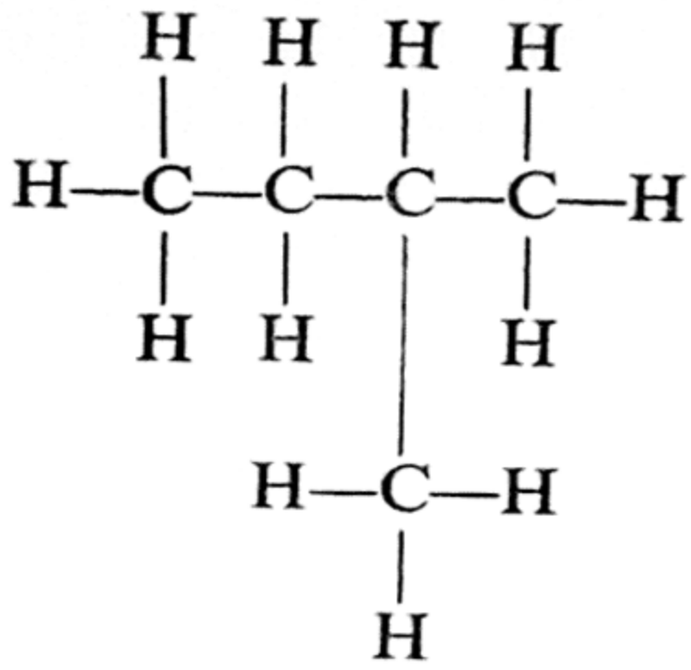
(*b*) The carbon atoms are able to link up together, apparently without limit save that the valency bond requirements must be satisfied, to form stable compounds.

Of these two properties, the first is not unique; elements such as silicon, tin and lead also have a normal valency of four, but, with the possible exception of silicon, these elements do not possess the second property. The importance of this second property appears more significant if one considers the hydrogen compounds of oxygen, namely, water with the structure H—O—H and hydrogen peroxide with the structure H—O—O—H. Clearly the linkage of oxygen to oxygen so decreases the stability of the molecule that a possible third compound in the series with the structure H—O—O—O—H does not exist. With carbon such a decrease in the stability does not occur, and complex molecules, having a long chain, a branched chain, or even rings of carbon atoms, together with various combinations of these, can and do exist. If we consider the hydrocarbons, that is, compounds containing only carbon and hydrogen, examples of such complex molecules might include—

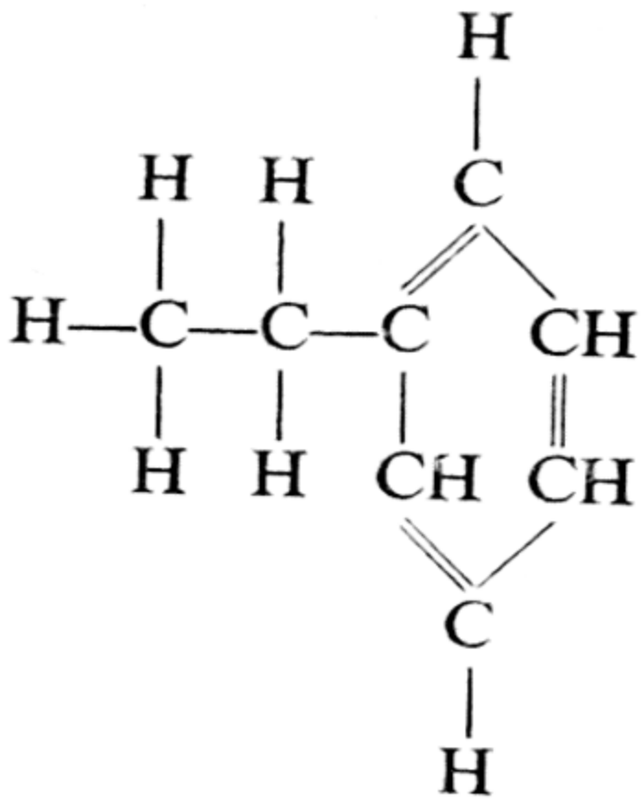
Octane



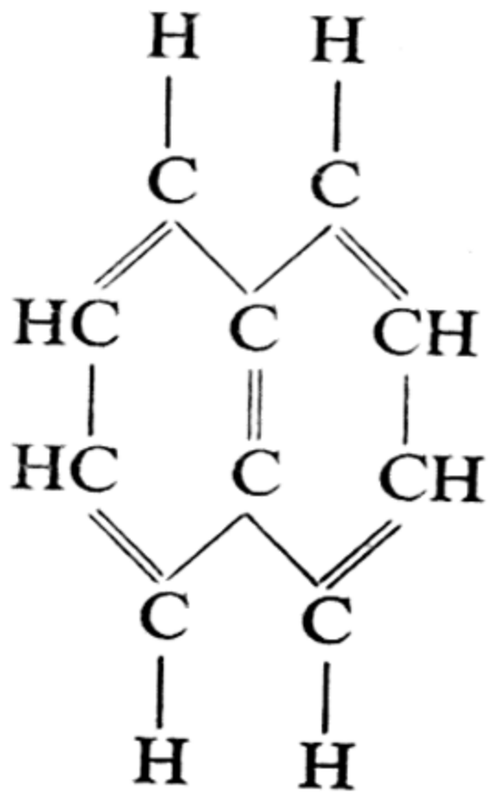
Iso-pentane



Ethyl benzene

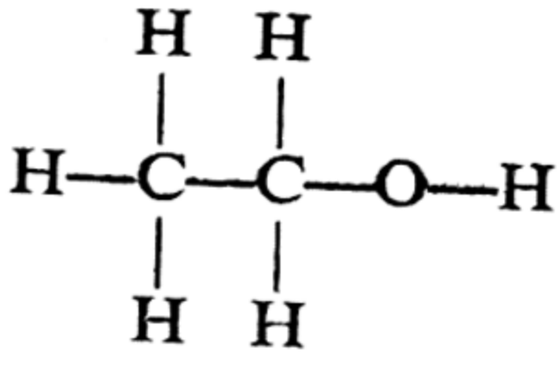


Naphthalene

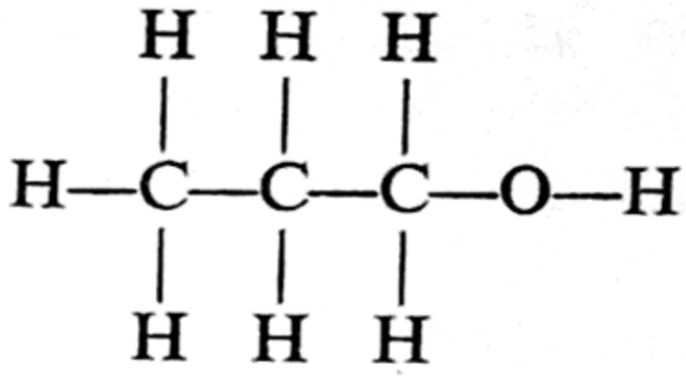


CLASSIFICATION OF ORGANIC COMPOUNDS

Ethyl alcohol and propyl alcohol have the structures,



and



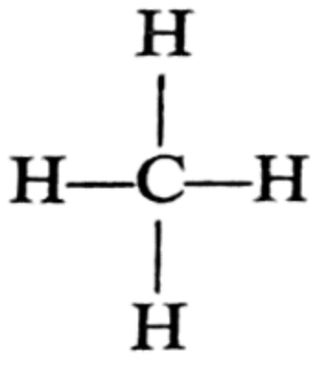
respectively. It will be observed that in each case the molecule may be regarded as composed of—(*a*) the carbon or hydrocarbon portion, and (*b*) the O—H portion. Variation in the hydrocarbon chain, involving an increase or decrease in the number of carbon atoms, does not appreciably modify the alcoholic properties imparted to the molecule by the hydroxyl group, *but* if this latter group be changed for any other univalent group, such as the amino-group, NH_2, then a very profound change in properties results. We thus recognize for the purpose of classifying and systematizing the study of organic chemistry, the need in the first place to study the possible arrangements of the carbon atoms in the hydrocarbon portion of the molecule, and then to study the properties imparted by the substituent groups (—OH, —NH_2, —CHO, etc.) to these hydrocarbons.

The hydrocarbons may be divided into two main classes—

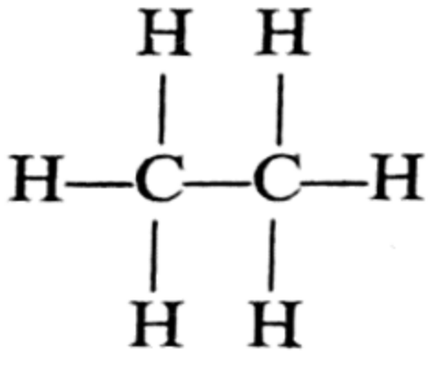
The *aliphatic* (or *chain*) compounds, and the *aromatic* (or *ring*) compounds, as exemplified by—

Aliphatic compounds

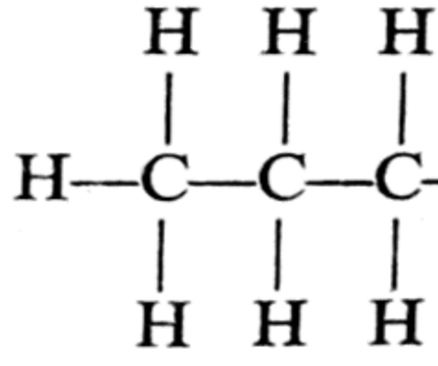
Paraffins



methane

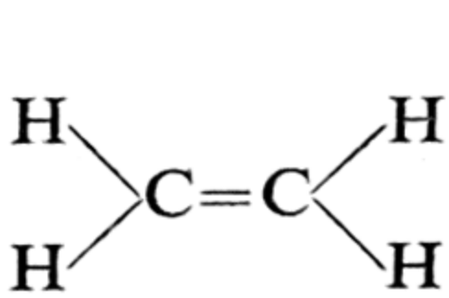


ethane

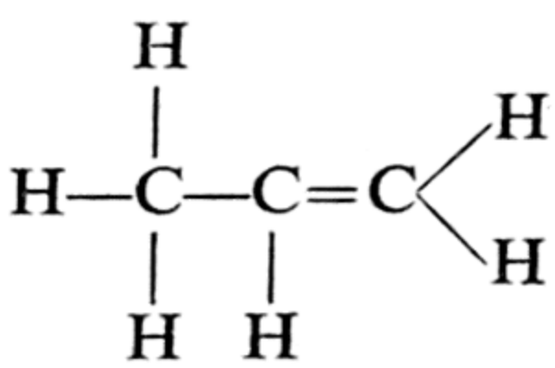


propane, etc.

Ethylenes

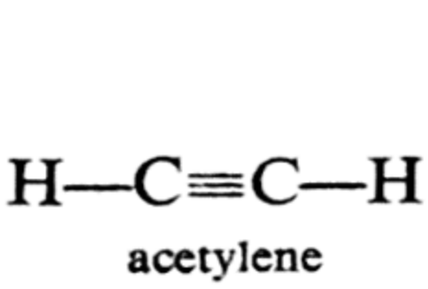


ethylene

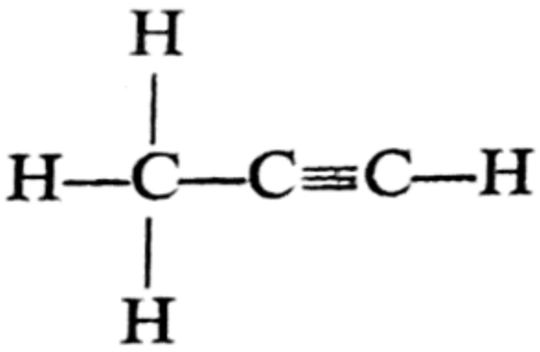


propylene

Acetylenes

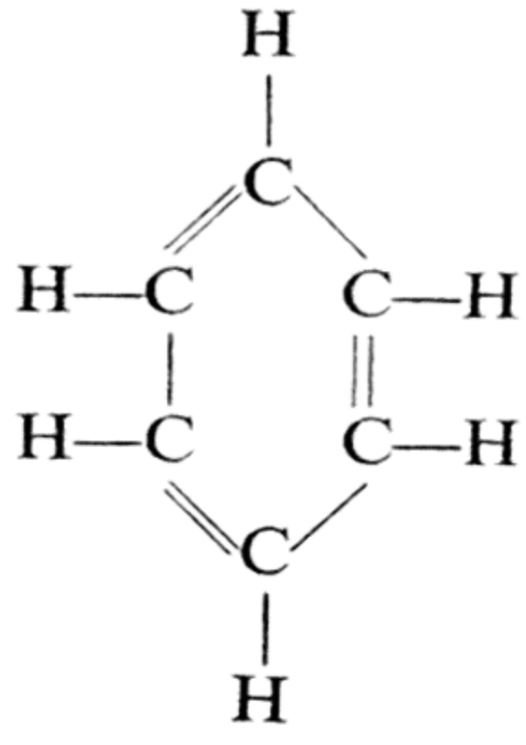


acetylene

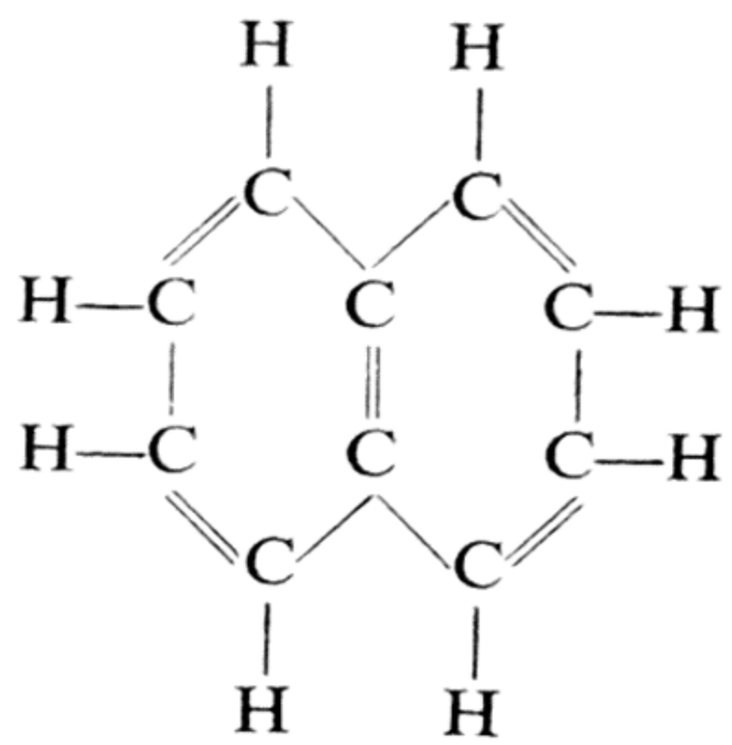


propine

Aromatic compounds



benzene



naphthalene

The names aliphatic and aromatic were suggested, on the one hand by the occurrence of the chain hydrocarbon structure in natural fats, and on the other by the aromatic odour associated with most of the ring compounds.

When one or more of the hydrogen atoms of these hydrocarbons are replaced by other elements or groups of elements (known as substituent groups), the resulting compounds have properties which are identified with and determined by the particular substituent group. Thus, replacement of a hydrogen atom by—

The —OH, hydroxyl, group produces the alcohols.

The —CHO, aldehyde, group produces the aldehydes.

The —COOH, carboxyl, group produces the organic acids, and so on.

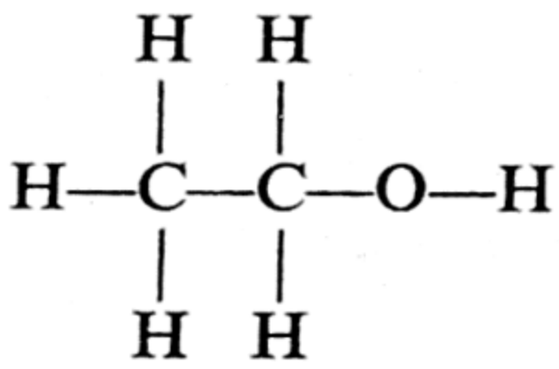
The study of organic chemistry thus begins properly with the study of the hydrocarbons and follows with the investigation of the substitution compounds.

Homologous Series. The series of compounds having the formulae CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, etc. is said to constitute an homologous series. When the compounds are arranged in this way in order of increasing molecular complexity it is seen that each compound differs from the preceding compound in having one extra carbon and two extra hydrogens, that is, in having an additional CH_2 group. Another such series would be; CH_3OH, C_2H_5OH, C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$, etc. Each such homologous series has its own characteristic chemical and physical properties, properties which are shared by each member of the series. Ascent of the series, that is, in the direction of increasing molecular weight, is accompanied by small progressive changes in the physical properties; thus, the boiling-points and melting-points gradually increase, whilst the solubility decreases. The chemical properties however change much less markedly.

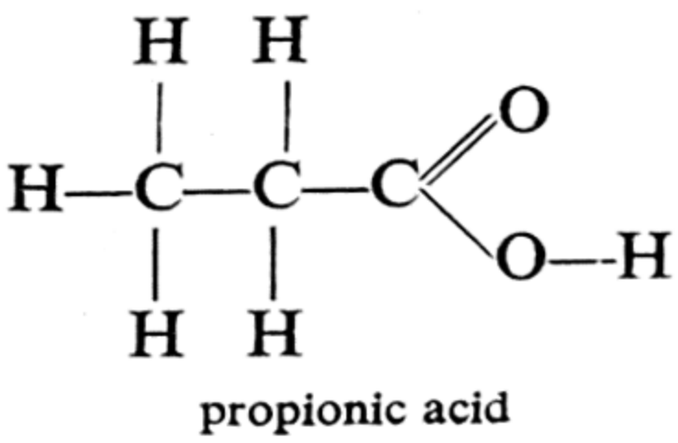
If the chemistry of the simpler members of each homologous series is well understood, that of the more complex members of the same series may usually easily be deduced. The study of organic chemistry, in its second

phase, thus resolves itself into the study of the simpler compounds of each possible homologous series, a procedure which enormously reduces the complexity of the subject. Of the 250,000 organic compounds known to exist, the average organic chemist may be familiar only with several hundred of them, the simpler members of each series. This limited knowledge coupled with the further knowledge of how these compounds may be prepared and used to prepare other compounds, provides him with the material for a working knowledge of them all.

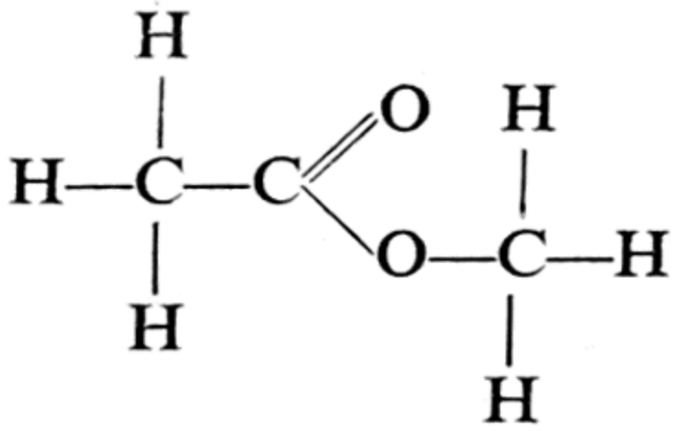
Structural Formulae. Structural formulae, as the name implies, reveals the way in which the various atoms arrange themselves to form the molecule of the organic compound. Thus ethyl alcohol with a molecular formula of C_2H_6O has the structural formula



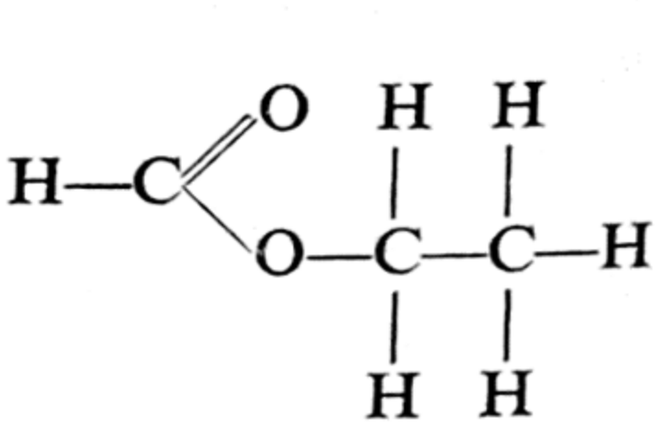
This method of picturing the molecule shows, for example, that one of the hydrogen atoms is linked to oxygen and so will probably have different properties from those of the other five which are linked to carbon atoms. This method of depicting organic compounds by their structural formulae, as opposed to their molecular formulae, satisfies the need of the chemist to see at a glance the arrangement of the carbon atoms and the position taken up in the molecule by the substituent group(s). In particular it explains the existence of numerous compounds which have the same molecular formula but which possess quite different properties. Thus, the molecular formula $C_3H_6O_2$ may refer to—



propionic acid



methyl acetate



ethyl formate

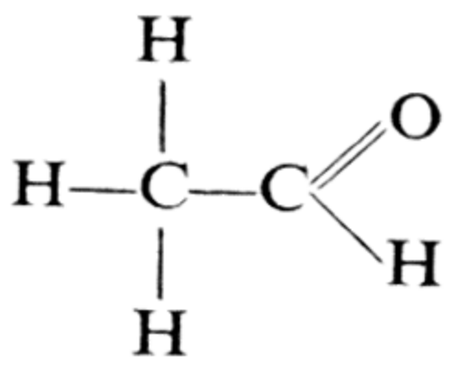
When no ambiguity arises, these structural formulae may be abbreviated to $C_2H_5 . COOH$, $CH_3 . COOCH_3$, and $H . COOC_2H_5$ respectively. This phenomenon in which one molecular formula may represent two or more different compounds is known as *isomerism*, a fuller discussion of which is deferred until later in the text.

Two facts should be appreciated by the student before attempting to write structural formulae. These are—

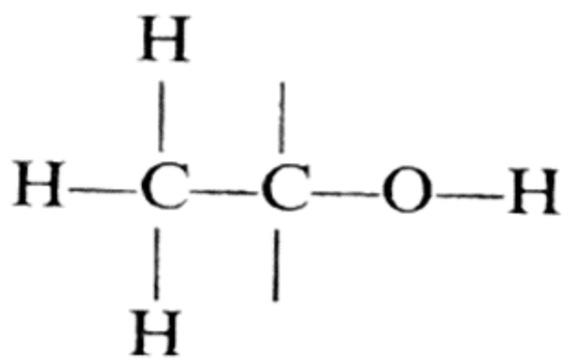
(*a*) The four valency bonds from each carbon atom have a regular

spacial (tetrahedral) arrangement. It is not however always convenient to observe this fact when writing formulae, and the convention has grown up whereby the valency bonds from each carbon atom are depicted as square planar, thus rather than tetrahedral, thus . This convention is however only one of convenience; it should not be interpreted as implying that the four valency bonds from each carbon atom are actually planar.

(*b*) The rules of valency must always be strictly observed when writing structural formulae. Each of the four carbon valency bonds must always be directly involved in the resulting structural formula of the molecule and the valency requirements of the other atoms in the molecule must also be satisfied. Thus the compound C_2H_4O has the structure



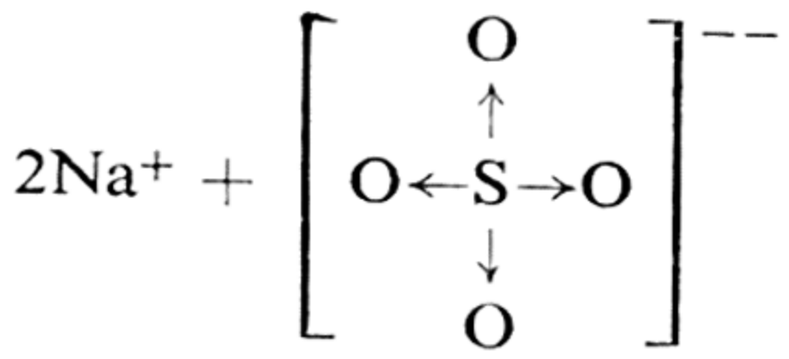
acetaldehyde

but *not* 

since one of the two carbon atoms would have two free valency bonds.

Covalency and Organic Chemistry. There remains to be discussed one important distinction between organic and inorganic chemistry before this introductory chapter to organic chemistry can be considered complete. Most of the reactions of organic chemistry occur relatively slowly, whereas most inorganic reactions occur immediately on mixing the appropriate solutions. In organic chemistry it is usually necessary to heat the reacting substances together for some time before any appreciable reaction occurs. The reason for this reluctance of most organic compounds to react instantaneously is to be found in the nature of the valency bonds involved in their molecular structure.

Two principal types of valency bond have been described (*see* p. 68), i.e. electrovalency and covalency. Inorganic compounds are usually either electrovalent or both electrovalent and covalent; thus sodium sulphate has the structure



Most of the reactions in inorganic chemistry occur between ions, e.g. Na^+ and $(SO_4)^{--}$, and so do not involve any cleavage of the covalent

portion of the molecule. Such reactions in general occur instantaneously since the ions are already present as such in the aqueous solutions. In most organic reactions, no ionization of the reacting molecules occurs since they are entirely covalent. Before any appreciable reaction can occur with such compounds, some dissociation or splitting up of the molecule must occur. Increasing the temperature of the reaction has the effect of increasing the energy of the molecules, a portion of this increased energy being absorbed by increased energy of vibration of the atoms relatively to each other in the molecule. This increased vibrational energy eventually leads to some dissociation of the molecule at its weakest linkage, and the two portions of the molecule so produced, known as *free radicals*, may then react with the other compound present. Since the proportion of molecules so tending to dissociate increases with temperature, further increase in temperature should produce a further increase in the rate of the reaction. Most organic reactions consequently only occur on prolonged heating, and are often carried out at the maximum possible temperature determined by the boiling point of the more volatile reactant. The dissociation envisaged as preceding the reaction may also occur in the ionic sense, in which the neutral covalent molecule undergoes a slight degree of ionization into free ions. Both mechanisms are correct, but the conditions under which they apply depend on other factors such as the nature of the reaction and the type of solvent being used. Sufficient has, however, been said at this stage for the student to appreciate that, in general, organic chemistry is associated with slow reactions.

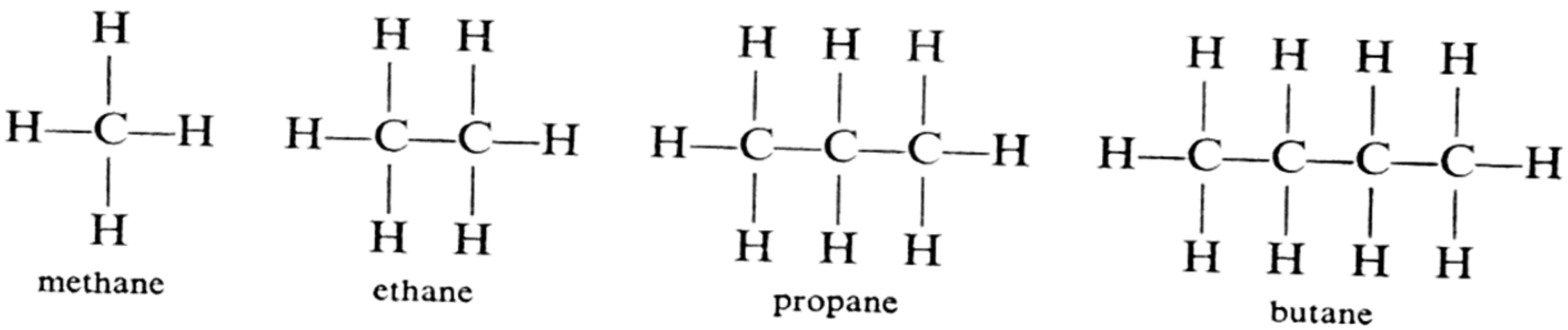
CHAPTER 28

PARAFFIN, OLEFINE AND ACETYLENE HYDROCARBONS

It has been stated in the previous chapter that organic compounds may be classified into a number of homologous series, some of which are simple and others more complex.

THE PARAFFINS

The paraffin series, which forms the subject of the present chapter, is the simplest of these and is composed of compounds of carbon and hydrogen in which the various carbon atoms are linked by single bonds to the adjacent carbon atoms, as in the following examples—



For reasons which will be discussed later, these compounds are described as *saturated* hydrocarbons, to distinguish them from hydrocarbons, such as, ethylene, acetylene and benzene, which are *unsaturated.*

Methane, formula CH_4, is the first member of the *paraffin* series. It is a gas and occurs in considerable quantities in nature. The "natural gas" which escapes from oil-wells in certain parts of the world is very largely composed of methane. The "eternal fires" of Baku were caused by this same gas burning as it escaped through fissures in the rock above the Baku oil-deposits. In the U.S.A. much of this natural gas is now collected and distributed to domestic consumers as a substitute for coal gas. Coal gas itself may contain from 20–25 per cent of methane (together with hydrogen and carbon monoxide as the other principal constituents). Methane is also found in coal mines, where it is known as *fire-damp* and is responsible for most of the explosions that occur. The formation of methane, by the bacterial decomposition of vegetable matter in the absence of oxygen, sometimes causes bubbles of the gas to rise from stagnant ponds. This methane, or *marsh-gas* as it is sometimes called, if it contains traces of impure phosphine may ignite as it breaks the surface of the water and produce the phenomenon of "will o' the wisp."

Preparation of Methane. The usual laboratory method is to heat a mixture of anhydrous sodium acetate (prepared by heating crystalline

sodium acetate until fused) with soda-lime. Soda-lime is quick-lime which has been slaked with a concentrated solution of sodium hydroxide, and behaves virtually as a mixture of sodium hydroxide and calcium hydroxide.

$$CH_3 . COONa + NaOH = CH_4 + Na_2CO_3$$

Methane may also be prepared by the following methods—

By the action of water on aluminium carbide—

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3$$

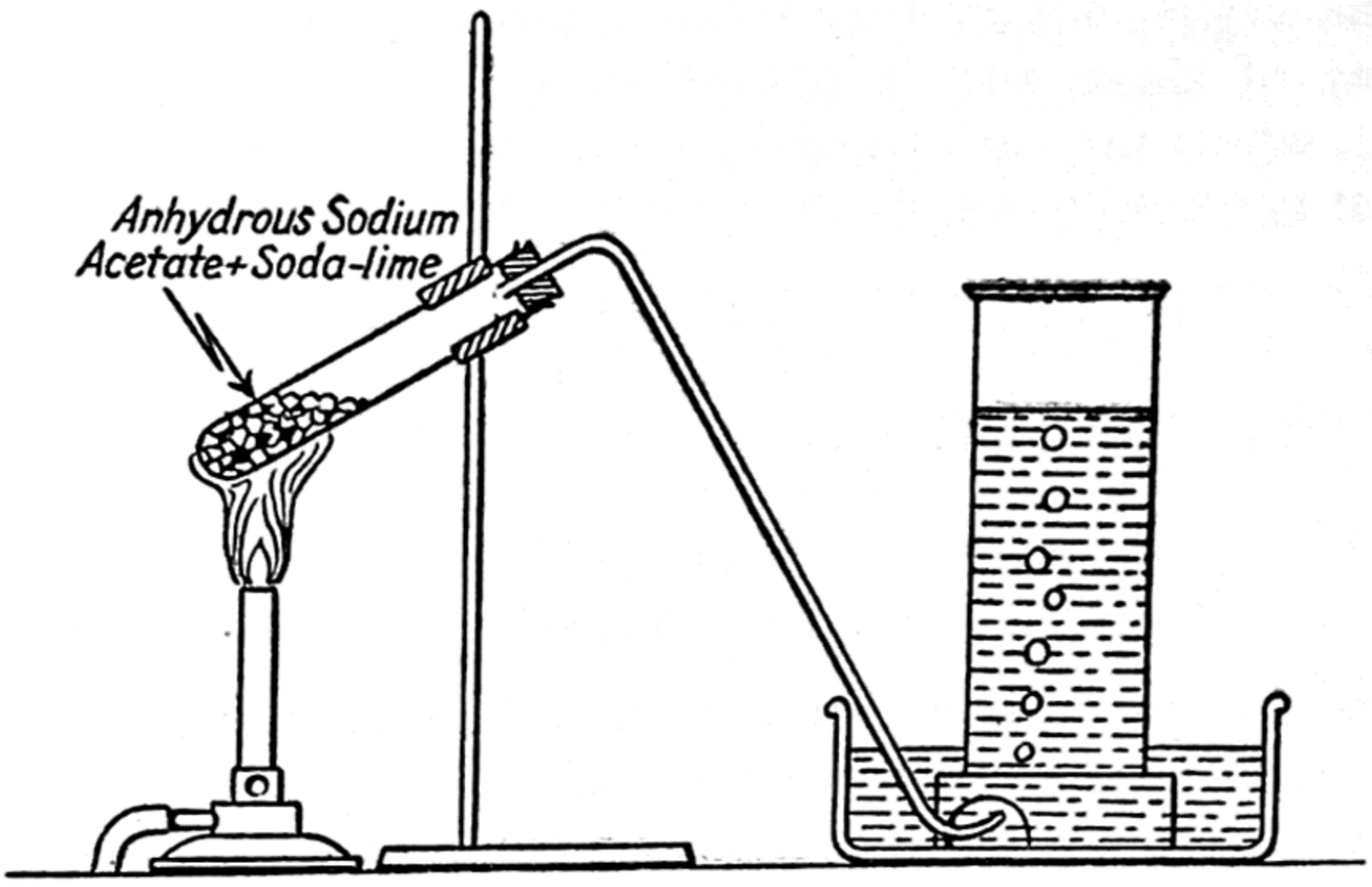


FIG. 252. Preparation of Methane from Sodium Acetate

By the reduction of methyl iodide with nascent hydrogen, produced for example in situ by the action of a zinc-copper couple on methyl alcohol.

$$CH_3I + 2H = CH_4 + HI$$

The zinc-copper couple may be prepared by immersing pieces of zinc in a solution of copper sulphate for a short time, or by heating copper powder with zinc foil in an atmosphere of coal gas until the mixture cakes together.

By the Sabatier and Senderens reaction in which a mixture of carbon monoxide (or dioxide) and hydrogen is passed over a finely-divided nickel catalyst at a temperature of about 250°C—

$$CO + 3H_2 = CH_4 + H_2O$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

Properties of Methane. Methane is a colourless, odourless gas, lighter

than air (8, cf. 14·4) and is practically insoluble in water. Chemically, it is relatively inert, and does not react with acids, alkalis, nor the common oxidizing and reducing agents. This lack of chemical reactivity which is characteristic of all the members of the paraffin series explains the name "paraffin," which means, literally, little affinity or reactivity.

The paraffins, however, are not completely devoid of chemical reactivity as the following important reactions show—

(*a*) *They Burn in Air or Oxygen.* Methane, for example, burns in air with a pale-blue, non-luminous flame—

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

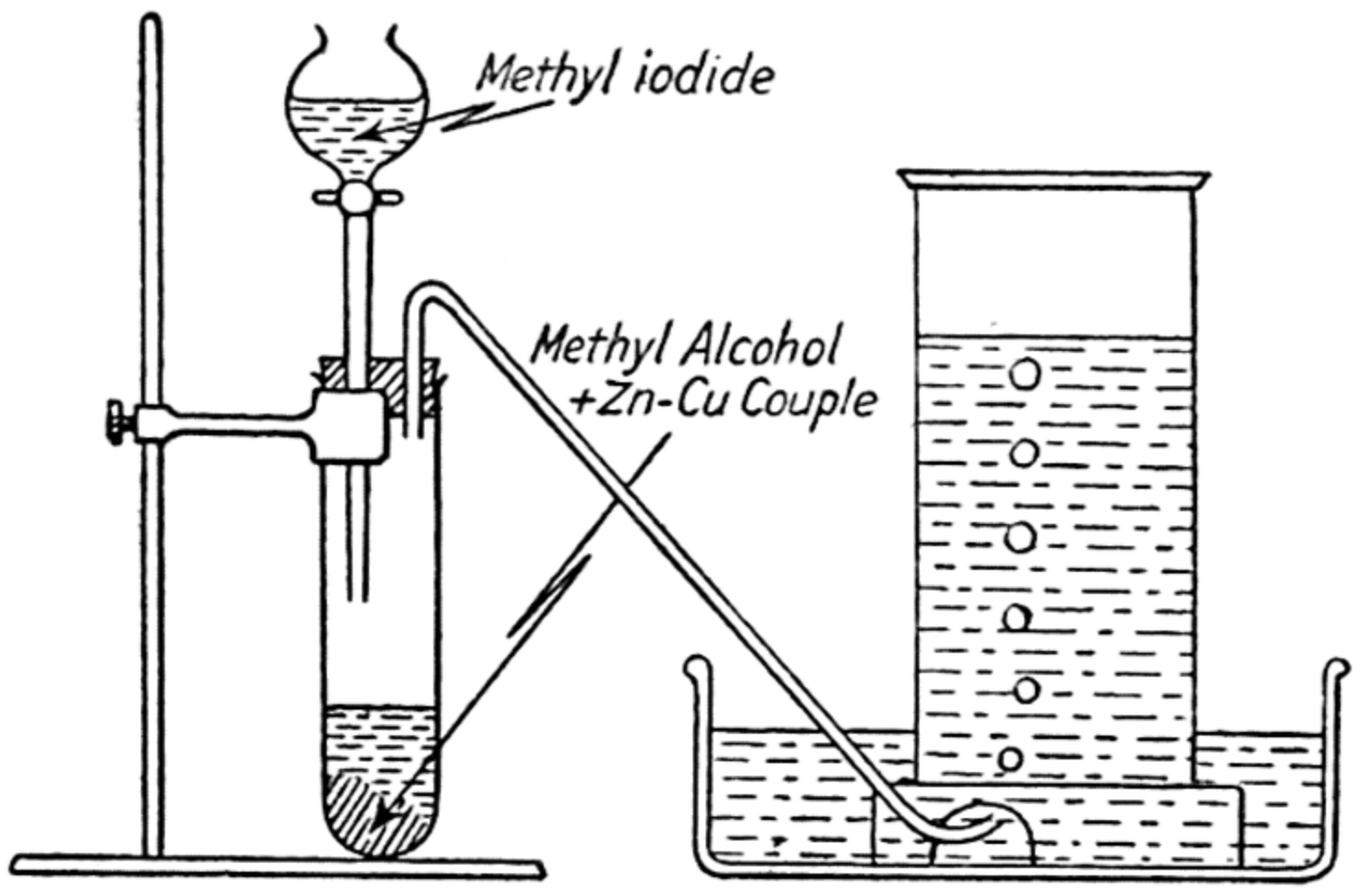


FIG. 253. Preparation of Methane from Methyl Iodide

Within certain limits of composition, mixtures of paraffin gases and air (or oxygen) explode when ignited. Well-known examples of this explosive reaction include the accidental explosions which occur in coal-mines and the controlled explosions of petrol-vapour/air mixtures which provide the motive power in automobile engines. In these explosions, the oxidation of the methane or higher paraffin is often incomplete and much carbon monoxide is produced—

$$2CH_4 + 3O_2 = 2CO + 4H_2O$$

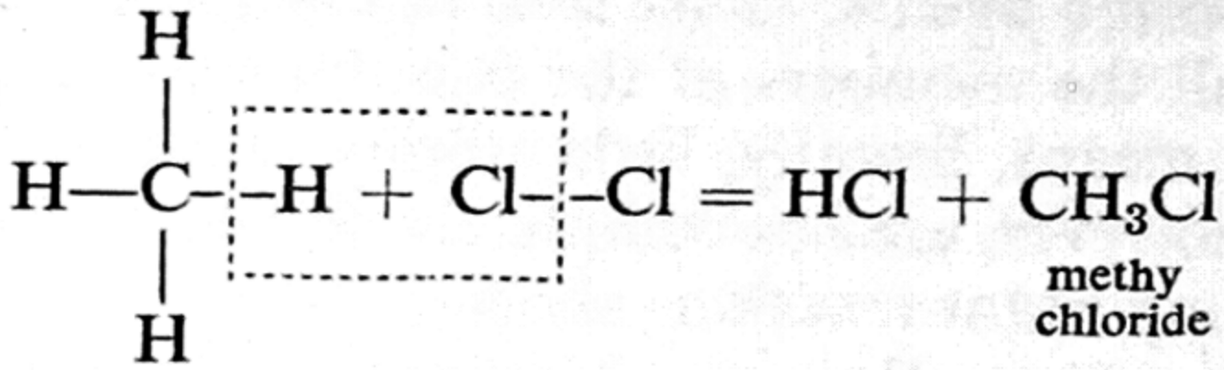
This carbon monoxide is the much feared "after-damp" in coal mines after explosions, and also explains the very poisonous nature of the exhaust gases from petrol engines.

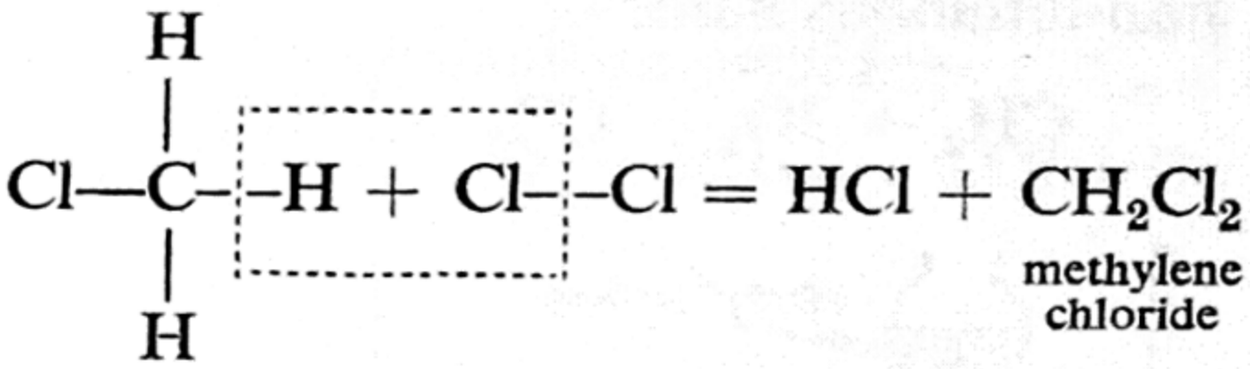
(*b*) *Reaction with Halogens.* Mixtures of methane and chlorine explode when ignited or when exposed to direct sunlight to deposit carbon and form hydrogen chloride gas—

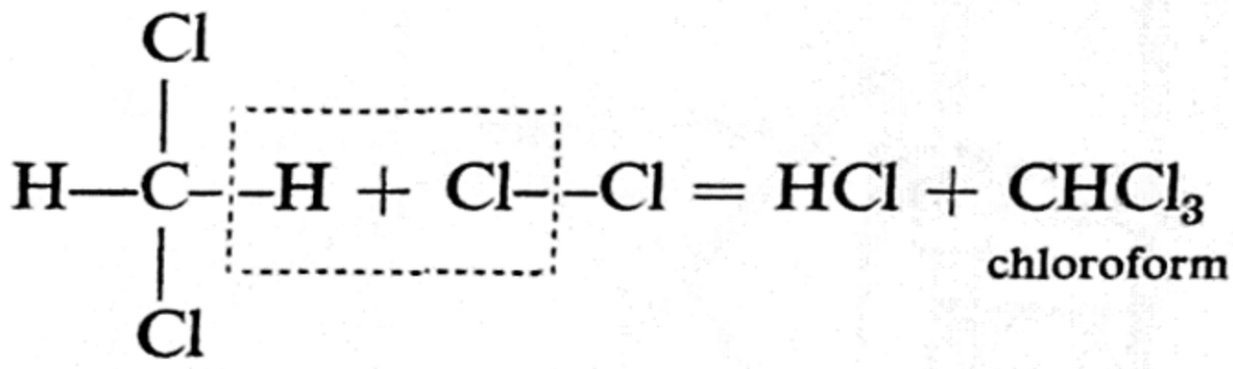
$$CH_4 + 2Cl_2 = C\downarrow + 4HCl\uparrow$$

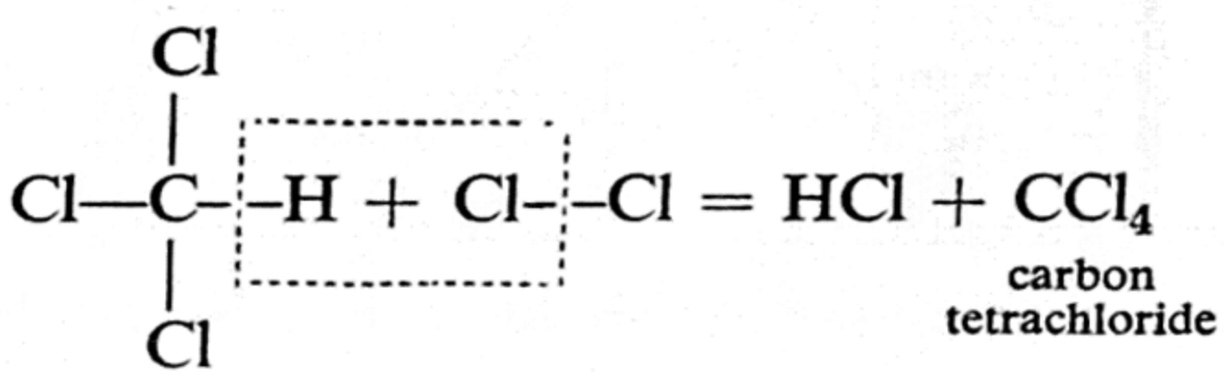
No reaction occurs when the mixed gases are exposed in the dark, but in

diffused sunlight a slower reaction occurs with progressive replacement of the hydrogen atoms by chlorine atoms—









These reactions in which one atom is replaced by a different atom are known as *substitution* reactions.

Similar reactions occur with bromine vapour, but the substitution occurs much more slowly, whilst iodine vapour shows little if any reactivity. Fluorine, on the other hand, reacts explosively with methane and other hydrocarbons due to its enormous affinity for hydrogen.

The Paraffin Series

The general formula of the members of the paraffin homologous series is C_nH_{2n+2}, i.e. CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, etc. Their melting points and boiling points increase progressively with increase in molecular weight, the earlier members being gases at ordinary temperatures, the intermediate liquid, and the heaviest members waxy solids like paraffin wax.

Methane	CH_4	b.p. $-164°C$	*Colourless gases*
Ethane	C_2H_6	b.p. $-93°C$	
Propane	C_3H_8	b.p. $-42°C$	
n-Butane	C_4H_{10}	b.p. $-0{\cdot}5°C$	

Pentane	C_5H_{12}	b.p. + 36°C	*Colourless liquids*
Hexane	C_6H_{14}	b.p. + 69°C	
Heptane	C_7H_{16}	b.p. + 98·4°C	
Octane	C_8H_{18}	b.p. + 125·6°C	
Heptadecane	$C_{17}H_{36}$	m.p. + 22°C	*Waxy-solids*
Octadecane	$C_{18}H_{38}$	m.p. + 28°C	
Pentatriacontane	$C_{35}H_{72}$	m.p. + 75°C	

General Methods of Preparation

1. By heating the sodium salt of a fatty acid (*see* p. 923) with soda-lime

$$C_2H_5 . \boxed{COONa + NaOH} = Na_2CO_3 + \underset{\text{ethane}}{C_2H_6}\uparrow$$

$$C_nH_{2n+1} . \boxed{COONa + NaOH} = Na_2CO_3 + C_nH_{2n+2}\uparrow$$

2. By reducing the corresponding alkyl iodide with nascent hydrogen, for example, via a zinc-copper couple and alcohol—

$$C_nH_{2n+1}I + 2H = C_nH_{2n+2} + HI$$

3. By the *Wurtz synthesis*, e.g.

$$\begin{matrix} CH_3 I \\ \\ CH_3 I \end{matrix} \boxed{\quad + 2Na \quad} = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + 2NaI$$

The reaction is carried out by adding sodium to a solution of the carefully dried alkyl iodide in ether. The free alkyl radicals, produced by the removal of the iodine atom, couple together to produce the stable paraffin. If a mixture of two alkyl iodides, R′I and R″I, be used the resulting paraffin will be a mixture of the three hydro-carbons R′–R′, R′–R″ and R″–R″. *Note* that the alkyl iodides are used instead of the corresponding bromides or chlorides because of their greater reactivity due to easier removal of the iodine atoms.

4. By *Kolbe's Electrolytic* method in which a concentrated aqueous solution of the potassium salt of a fatty acid is electrolyzed, e.g.

$CH_3 . COOK$ exists in solution as $(CH_3 . COO)^-$ and K^+ ions

Anode reaction: $(CH_3 . COO)^- \rightarrow (CH_3COO)$, followed by

$$\begin{matrix} CH_3 . COO \\ + \\ CH_3 . COO \end{matrix} \rightarrow \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + 2CO_2$$

If a mixture of two different potassium salts (R′ . COOK and R″ . COOK)

be electrolyzed in this way, the product is a mixture of the three hydrocarbons, R′–R′, R′–R″ and R″–R″.

5. From unsaturated hydrocarbons (*see* p. 872) by reduction with hydrogen, for example, by *the method of Sabatier and Senderens* (vapour plus hydrogen passed over finely divided nickel catalyst at about 250°C).

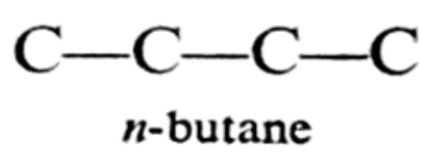
$$C_2H_4 + H_2 = C_2H_6$$
$$C_2H_2 + 2H_2 = C_2H_6$$

Properties of the Paraffins. As has already been noted, the paraffins are characterized by a lack of chemical reactivity. At ordinary temperatures, they do not react with nitric acid, fuming sulphuric acid, strong alkalis, metallic sodium, strong oxidizing agents such as chromic acid and potassium permanganate, and even at higher temperatures they may only react very slowly with these reagents. They do, however, react with the halogens (but *not* with iodine) to form substitution products, and also burn or form explosive mixtures with oxygen and air.

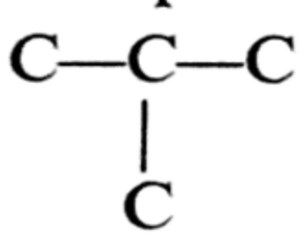
Isomerism in the Paraffin Series

Using the convention of depicting the four valency bonds from each carbon as planar, it is readily seen that, in addition to straight chain hydrocarbons, branch chain hydrocarbons may also occur, as depicted in the following carbon skeletons for butane and for pentane—

C_4H_{10}

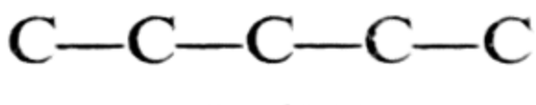


n-butane

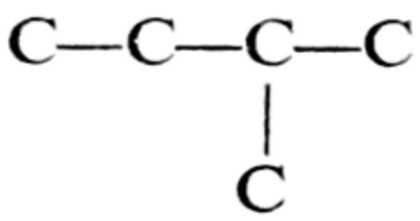


iso-butane

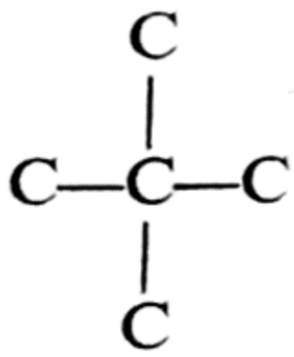
C_5H_{12}



n-pentane

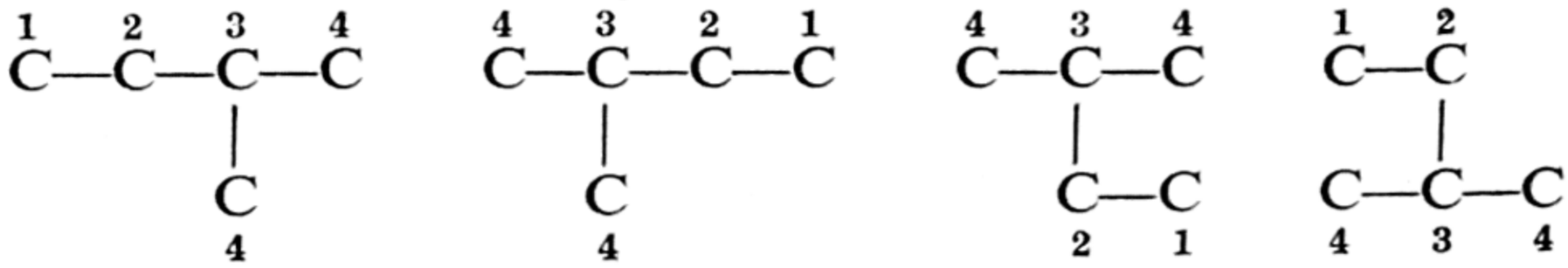


iso-pentane



neo-pentane

The student may at first find it difficult to appreciate that the following carbon skeletons are identical—



If in doubt, the procedure is to pick out the longest carbon chain, irrespective of whether the chain appears to be straight or otherwise, as in the preceding structures.

Substances which have the *same* molecular formula (e.g. C_5H_{12}) but different structural formulae (and, therefore, different properties, e.g.

n-pentane, iso-pentane, and neo-pentane) are said to be *isomers* and the phenomenon is known as *isomerism*. The number of different isomers possible in the paraffin series increases rapidly with increase in the number of carbon atoms in the molecule; thus decane, $C_{10}H_{22}$, has seventy-five different structural formulae, although it is safe to say that all these possible different isomers have never been isolated.

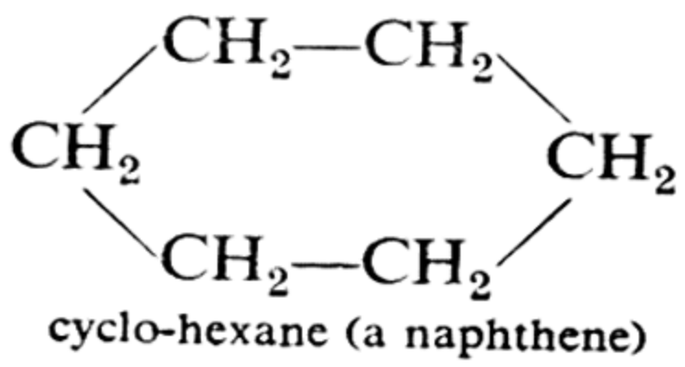
Alkyl Compounds. Organic chemistry is often described as the chemistry of the compound radical. Considering the mono-substitution products of the paraffins, these have the general formula, $(C_nH_{2n+1})X$, in which X may be any univalent atom or group of atoms. It is equally true to say that the group, C_nH_{2n+1} is also univalent, and since this group, or compound radical, as it is more usually known, remains unchanged in many of the reactions of the compound, $C_nH_{2n+1}X$, it may be regarded as a univalent atom R. The compounds, CH_3Cl, C_2H_5Cl, C_3H_7Cl, etc., may thus be represented by the formula RCl in which R is CH_3-, or C_2H_5-, or C_3H_7-, etc.

The univalent radicals, CH_3-, C_2H_5-, etc., are known collectively as *alkyl* groups, and individually as *methyl-*, *ethyl-*, *propyl-*, etc. The compound C_4H_9Cl would thus be butyl chloride.

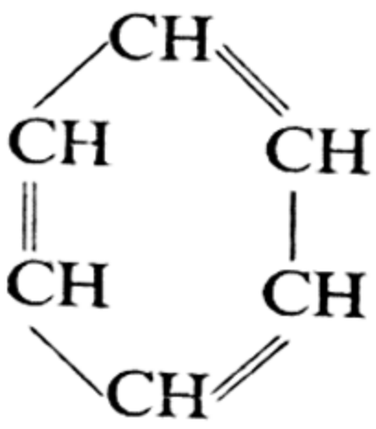
The divalent radicals, $CH_2=$, $C_2H_4=$, $C_3H_6=$, etc. are similarly known as *alkylene* groups, and the corresponding compounds as alkylene compounds, e.g. CH_2Cl_2 is known as methylene dichloride.

Other radicals which will be encountered in the study of organic chemistry include —OH, hydroxyl; >C=O, carbonyl; —CO . OH, carboxyl; —CO . CH_3, acetyl; —CHO, aldehyde; —NH_2, amino.

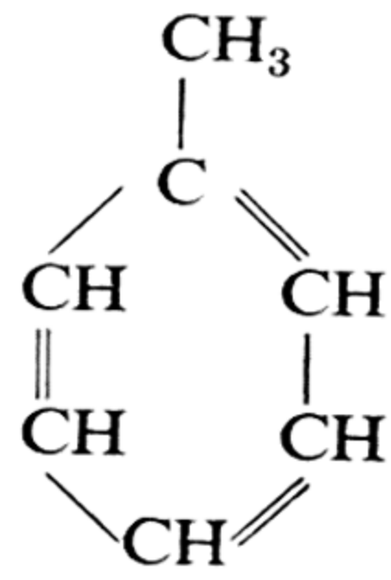
Petroleum. Crude petroleum consists essentially of various mixtures of gaseous, liquid, and solid hydrocarbons. These hydrocarbons belong not only to the paraffin or saturated hydrocarbon series but also to the cycloparaffins or naphthenes, to the benzene or aromatic hydrocarbon series and also to the unsaturated olefine hydrocarbon series. Examples of these other hydrocarbon series, the discussion of which is deferred to later in the book, include—



cyclo-hexane (a naphthene)



benzene



toluene

The nature of the crude oil varies with the part of the world in which it is found. There appear however, to be three principal varieties—

(*a*) *The Paraffin-base type* (or *Pennsylvanian type*), mainly paraffin hydrocarbons with smaller amounts of naphthenes and aromatic hydrocarbons (benzene, etc.)

(*b*) *The Asphaltic-base* (*or Caucasian*) *type*, mainly naphthenes with smaller quantities of paraffin and aromatic hydrocarbons, but relatively little wax.

(*c*) *The Mixed-Base* (*Galician or Rumanian*) *type*, mainly intermediate between the above two types and rich in solid waxes (higher paraffins, etc.).

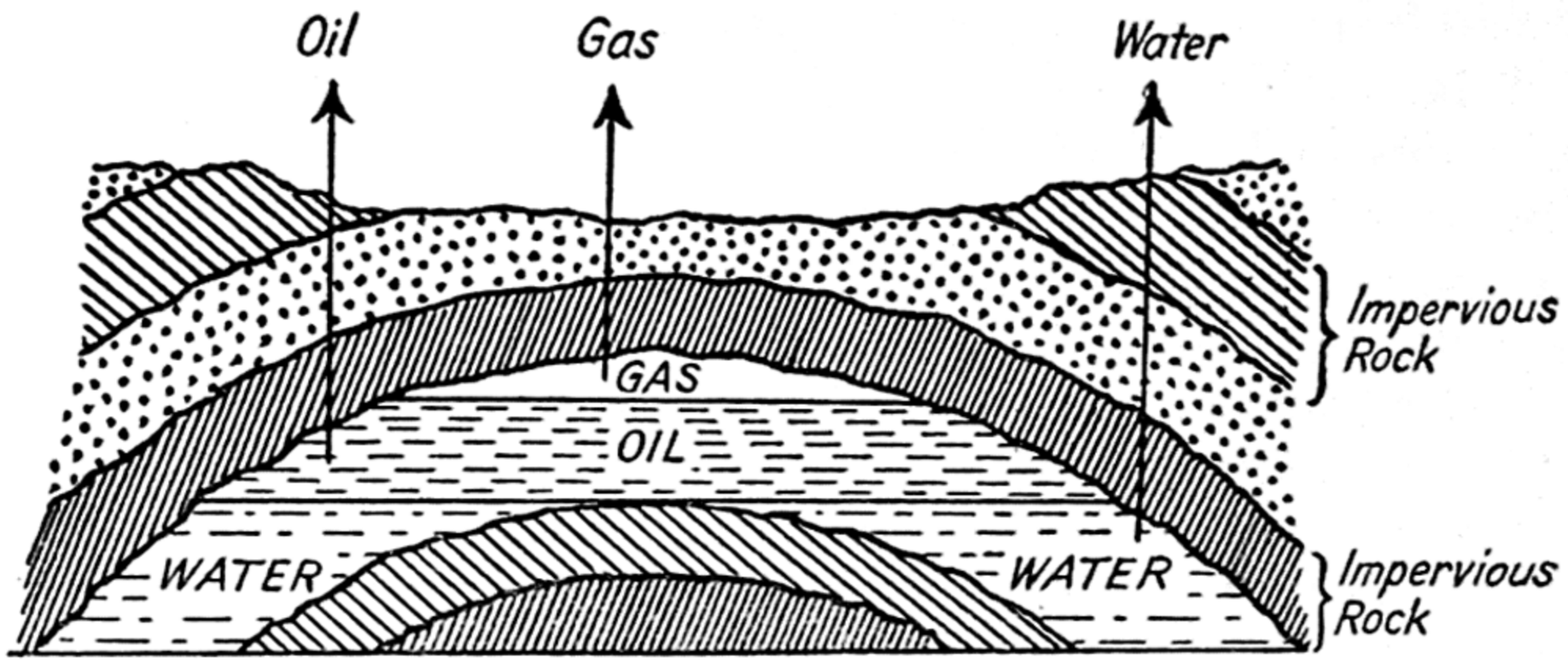


FIG. 254. Diagram showing a Typical Oil-well

Extensive deposits of petroleum occur in the areas covered by the above types, and in various parts of the U.S.A. (Oklahoma, California, etc.), Mexico, Iran and Iraq, Dutch East Indies, Rumania, Australia, etc.

Recovery and Treatment of Crude Petroleum. The accompanying diagram shows how crude oil and "natural gas" collect, in the course of time, in porous-rock strata which are so to speak insulated from above by strata of rock impermeable to oil. The crude oil is obtained by drilling through the impermeable rock layers to the porous rock which contains the crude oil. The diagram shows how the position of the boring, in relation to the distribution of the oil, may produce oil, or water and oil, or water or simply natural gas. If the boring is correctly sited, the oil is forced to the surface by the combined gas and water pressures. Later, as these pressures fall, it may be necessary to pump the oil to the surface, or even to flood the working to obtain any residual oil remaining in the well. When the oil reaches the surface, the resultant decrease in pressure leads to a dissolution of natural gas (methane, ethane, propane, etc.) dissolved in the oil, so that the crude oil appears as a dark-coloured foaming liquid. The gas, liquid and solid constituents are then separated by various mechanical separators.

Natural Gas. This is composed of the lower hydrocarbons, such as

methane, ethane, propane and butane. After treatment to recover most of the propane, butane and any higher hydrocarbons, the residual gas is distributed to industrial and domestic consumers through pipes, very much in the same way as is coal-gas.

Liquid Gas. The liquids recovered from natural gas are composed mainly of the hydrocarbons, propane, butane, propylene and butylene under pressure. They are distributed under pressure as the liquids for industrial and domestic heating purposes. "Calor-gas," marketed in this country, is somewhat similar. It is mainly composed of iso- and normal-butane, and is produced during the hydrogenation of coal at the Billingham plant.

Liquid Petroleum. Crude liquid petroleum is a complex mixture of a large number of different hydrocarbons, the complete separation of which would be extremely difficult and very costly. Instead of attempting such a complete separation, a partial separation is quickly and economically effected by the process of fractional distillation. In this way the oil is separated into a number of fractions having different boiling-point ranges. The number of fractions isolated depends upon the type of oil, but those included in the table shown on p. 868 are representative.

Motor Spirit or Gasolene, consists of a mixture of aliphatic, aromatic and naphthenic hydrocarbons boiling within a certain temperature range, which varies between certain specification limits. These specification limits vary with the power and type of petrol engine, and also with the season of the year. Thus motor spirit has a specification boiling-point range of 30°–200°C, whereas the limits specified for aviation spirit are 40°–180°C Commercial spirit is in reality a blend of a number of refinery products, the most important of which are—

1. Straight-run spirit: A fraction or "cut" from the distillation of crude petroleum.
2. Natural or casing-head spirit: A solution of higher boiling point hydrocarbons (from natural gas) in kerosene or gas-oil.
3. Cracked spirit: Obtained by cracking (*see* below) heavy-oil fractions.
4. Reformed spirit: Certain fractions within the boiling-point range of motor-spirit which are cracked to improve their anti-knock or volatility properties.
5. Polymerization spirit: By polymerization of various olefines produced during cracking operations.
6. Alkylation spirit: By combining lower paraffins with olefines in the presence of a suitable catalyst.
7. Hydrogenated spirit: By hydrogenating cracked or polymerized spirits which contain a large percentage of unsaturated hydrocarbons.

Blending is necessary to produce motor-spirits which have properties within certain specified limits as required by the modern motor-car engine. Such properties include boiling-point range, volatility, anti-knock rating, etc. One method of assessing and comparing motor-spirits is

TABLE 114

Primary Distillation Products from Crude Petroleum

General Name of Fraction	Special Fractions or Blends
Naphthas (30°–200°C) . .	Petroleum ethers Solvent naphtha (40°–70°C) Aviation spirit (40°–180°C) Motor spirit (30°–200°C) Commercial solvents
Kerosene (140°–315°C) . .	Lamp and stove fuel (160°–300°C) Motor fuel (140°–270°C) Signal oils Turpentine substitutes (white spirit)
Gas oils (180°–390°C) . .	Household-heating fuels Light industrial fuels Diesel fuel oils (190°–350°C)
Lubricating oils	These include such oils as; white, spindle, textile, cutting, transformer, compressor, refrigerator, journal, motor, compounded, valve, turbine, tempering, transmission, and railway oils Waxes, e.g. candle wax, medicinal wax, insulation wax, etc. Petroleum jelly (salves, creams, etc.)
Fuel oils	Wood preservatives Boiler fuel Metallurgical oils
Asphalts	Road emulsions Paving asphalts, water-proofing and insulating asphalts Emulsion bases, paint bases Rubber substitutes

based on the so-called "octane number." This is defined as the percentage by volume of iso-octane (2 . 2 . 4 tri-methyl pentane) in a mixture of iso-octane and normal pentane (a very poor motor-spirit) which matches the fuel being tested as to its "knock" or detonation characteristics when compared by a specified procedure knock-testing engine. In this test pure iso-octane gives an Octane Number of 100, normal heptane one of 0 and a

mixture of these two give intermediate values. If a given fuel shows a better rating than iso-octane (and some do), its octane number is taken as greater than 100.

Kerosene was formerly employed primarily for heating and illuminating purposes, and also as commercial solvents. Other products within the kerosine boiling-point range (140°–315°C) include turpentine substitutes (white spirit), tractor vaporizing oil (T.V.O.) and gas-absorption oils (e.g. used in preparing natural or casinghead spirit). The development of the jet-engine, however, has resulted in an enormously increased demand for kerosene. It is true that jet-engines may be designed to burn almost any grade of oil-fuel, but kerosene is preferred for aeroplanes because of the reduced risk of fire. Formerly, the demand for kerosene and its various products did not keep pace with the quantities obtained in the refining of crude petroleum, so that much of it was converted by cracking operations into lower-boiling hydrocarbons suitable for motor spirit. Now, the position is changed, and the world faces a shortage of kerosene.

Gas Oil, Diesel Fuel. Gas Oil is a rather indefinite term usually applied to petroleum fractions having viscosity and boiling-point ranges intermediate between those of kerosene and lubricating oils. It is employed as domestic or commercial fuels, for the manufacture of artificial gas (hence its name), and for conversion into motor spirit by cracking. It is also used as a fuel for certain types of Diesel engines, especially the high-speed types.

Cracking. The demand for more and more petrol led to the development of the *cracking* process for converting into petrol the heavier oil fractions obtained during the refining of crude oil. Cracking is essentially a process of thermal decomposition leading to simpler hydrocarbons with lower boiling-points, e.g.

$$\underset{\text{paraffin}}{C_{10}H_{22}} \xrightarrow{\text{"cracking"}} \underset{\text{paraffin}}{C_5H_{12}} + \underset{\text{olefine}}{C_5H_{10}}$$

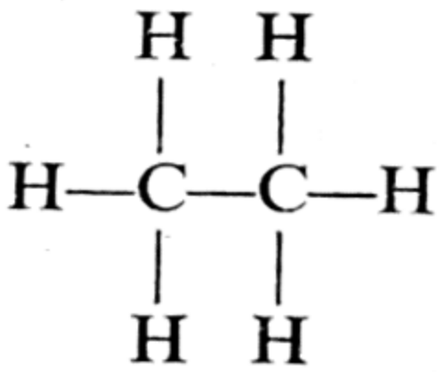
The process is carried out by heating the oil under pressure and may be carried out either in the liquid phase, or in the vapour phase. In the former, any type of oil, from residues and fuel oils to kerosenes, can be cracked, whilst the latter process is suitable only for those oils which may readily be vaporized.

For *Petrol from Coal*, *see* Chapter 22, p. 594.

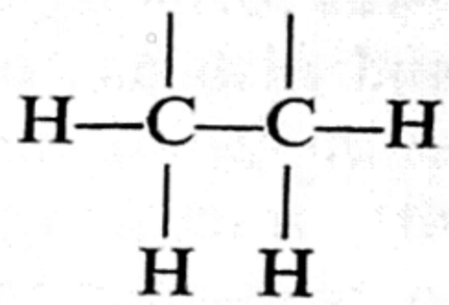
THE OLEFINE HYDROCARBONS

The olefine hydrocarbons are characterized by the presence in their molecules of a so-called *double bond*. The simplest member of the series, ethylene, for example, has the molecular formula C_2H_4. The corresponding

paraffin or saturated hydrocarbon, ethane, has the molecular formula C_2H_6, so that ethylene contains two less hydrogen atoms than ethane.



ethane



ethylene

For reasons which will be discussed later in this chapter, the two free

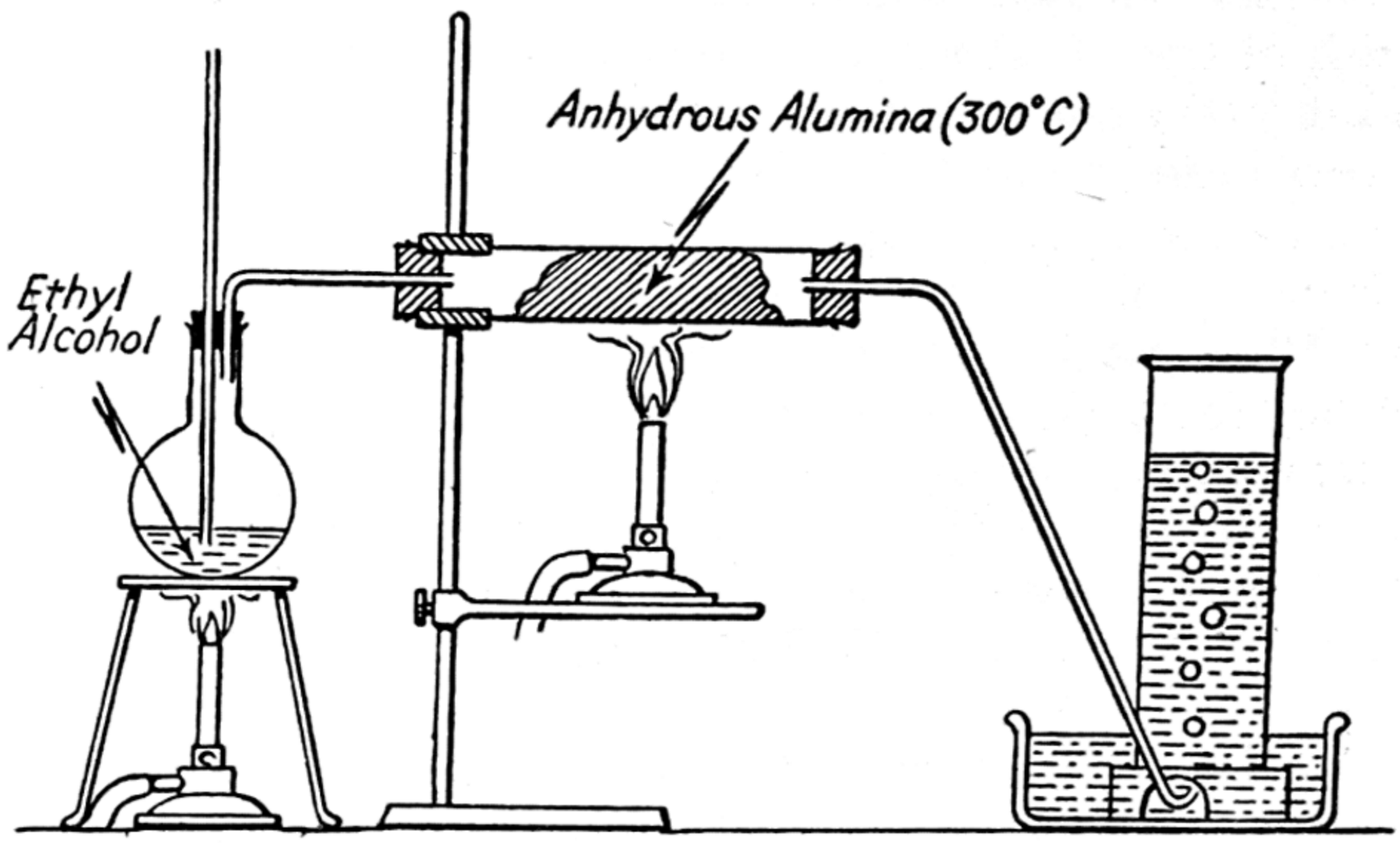
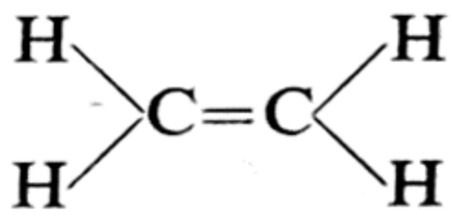


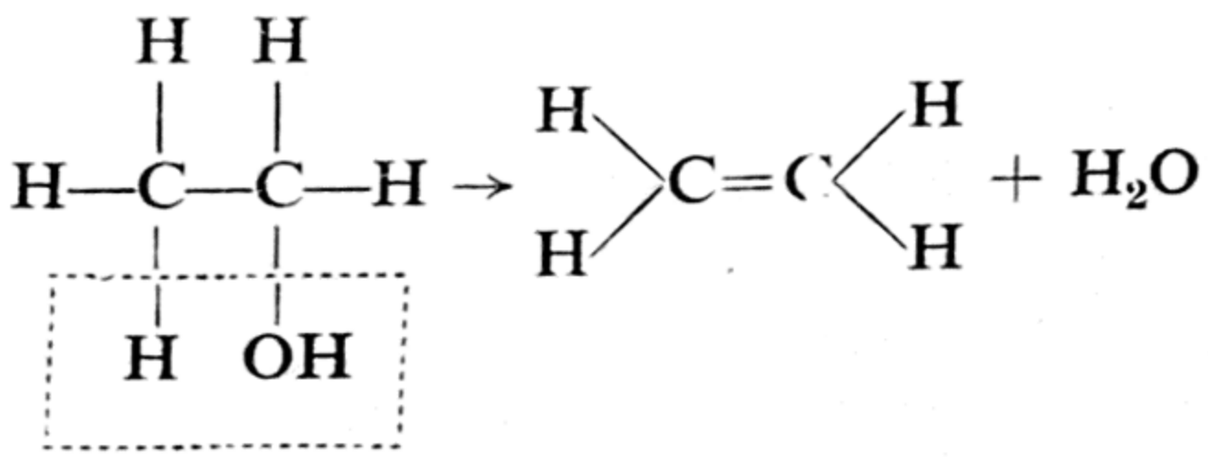
FIG. 255. Preparation of Ethylene from Ethyl Alcohol with Anhydrous Alumina as Catalyst

carbon valency bonds are regarded as forming an additional bond between the two carbon atoms, and the structural formula of ethylene is written as



in which the two carbon atoms are linked together by a double bond.

Preparation of Ethylene. This is effected by removing the elements of water from ethyl alcohol—



The reaction may be carried out in various ways—

(*a*) By passing ethyl alcohol vapour over anhydrous alumina (aluminium oxide) heated to about 300°C. The alumina appears to act catalytically.

(*b*) By heating ethyl alcohol with excess of concentrated sulphuric acid to 160°C. The preparation may be carried out in the apparatus shown below.

To about 20 ml of ethyl alcohol in the flask are cautiously added with cooling and shaking about 40 ml of concentrated sulphuric acid, followed by a little dry sand to assist the subsequent evolution of ethylene. (*Note*—the same care must be taken in adding concentrated sulphuric acid to alcohol as is observed on adding this acid to water.) The flask is then heated on a sand bath as shown in the diagram. The wash-bottle containing

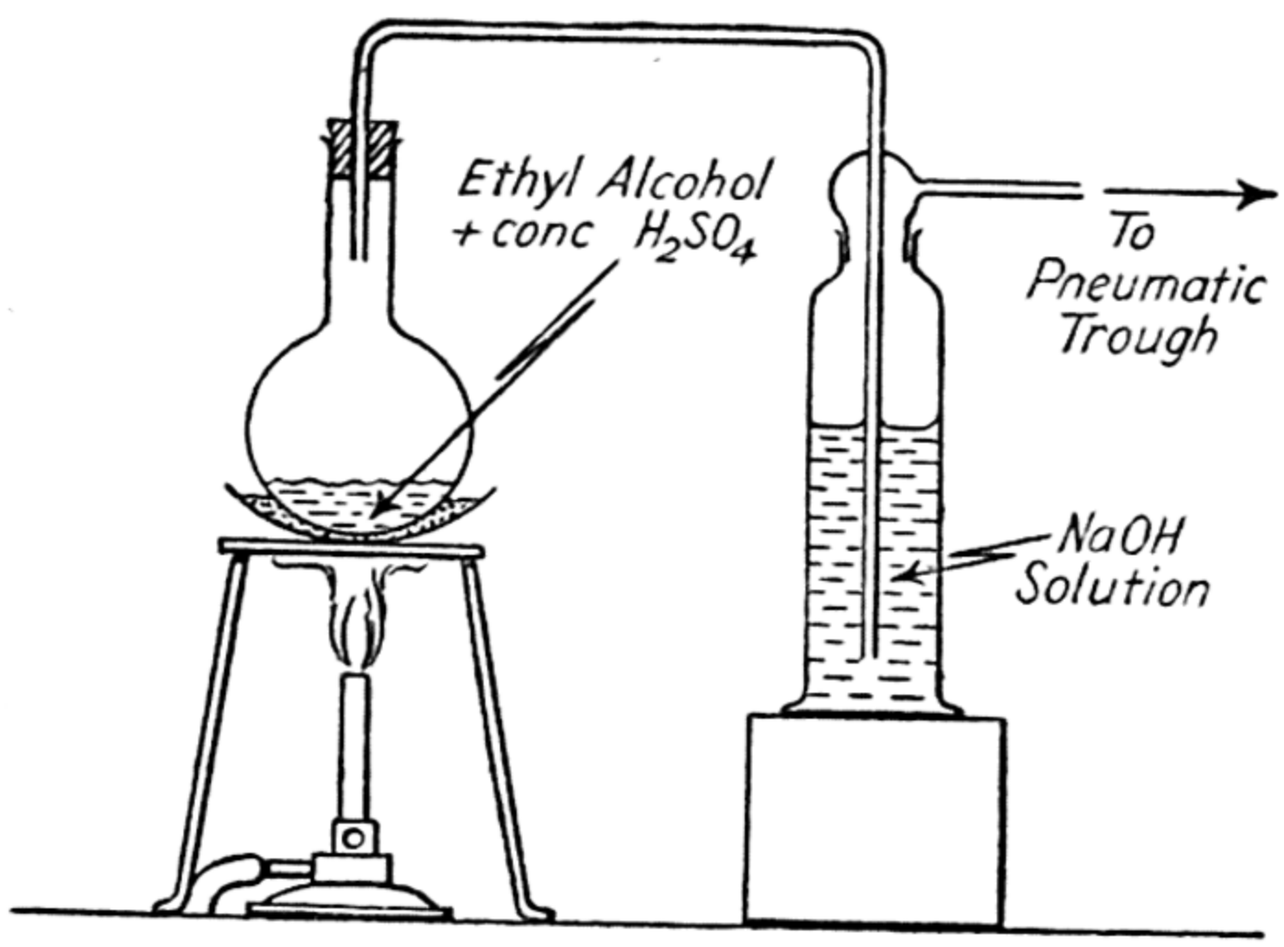


FIG. 256. Preparation of Ethylene from Ethyl Alcohol with Concentrated Sulphuric Acid

a solution of sodium hydroxide serves to remove any sulphur dioxide gas evolved in the process, and the ethylene is collected over water in the usual way. At the conclusion of the preparation the flask should be disconnected from the wash-bottle (to prevent suck-back) *before* removing the source of heat.

(*c*) A purer ethylene is produced by using syrupy phosphoric acid in place of the concentrated sulphuric acid in the above preparation, the ethylene being evolved at about 210°C.

A convenient laboratory method is to pass ethyl bromide vapour through a hard-glass tube containing soda-lime heated to a dull red heat.

$$C_2H_5Br + NaOH = C_2H_4 + NaBr + H_2O$$

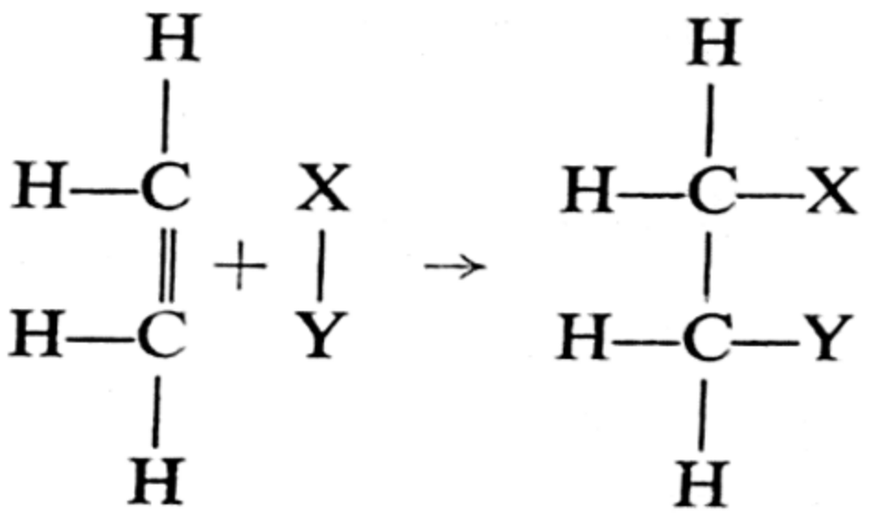
This preparation is a modification of the standard method for preparing high olefines by heating the alkyl iodide with an alcoholic solution of potassium (or sodium) hydroxide (*see* p. 877).

$$C_nH_{2n+1}I + KOH = C_nH_{2n} + KI + H_2O$$

Properties of Ethylene. Ethylene is a colourless gas with a characteristic faintly-sweetish odour. When deeply inhaled, it produces temporary anaesthesia without unpleasant after effects and is used for this purpose in dental surgery and in minor operations. It is practically insoluble in water but is appreciably soluble in other hydrocarbons.

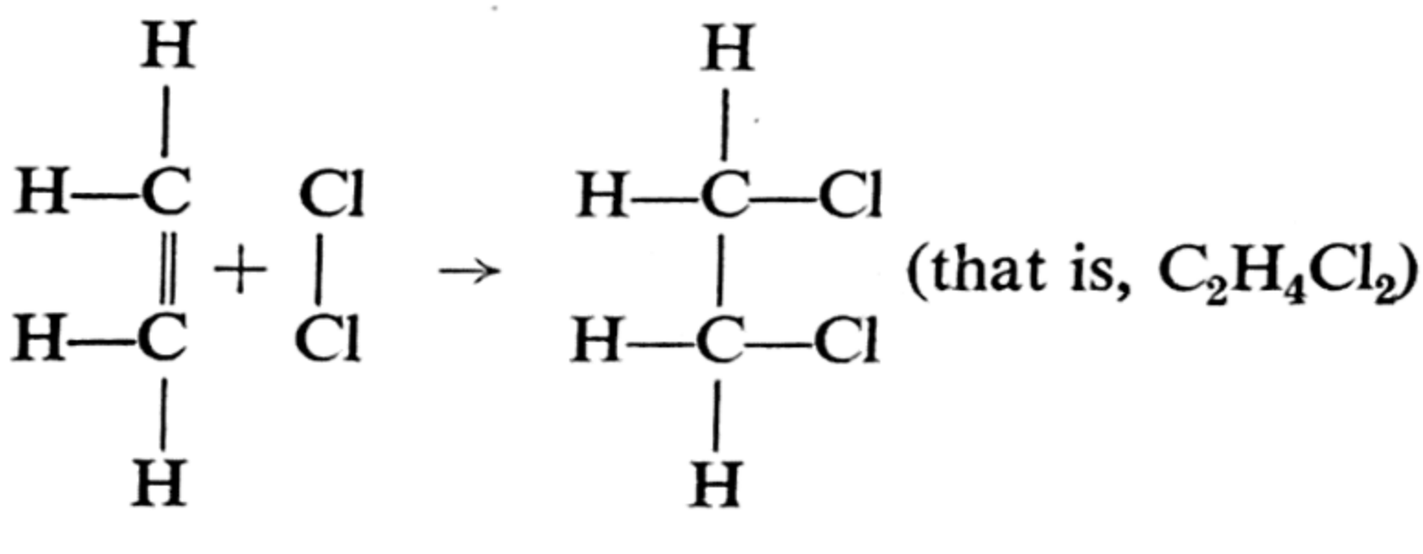
Ethylene burns in air with a clear pale-blue (almost invisible) flame and forms explosive mixtures with air and oxygen. In these reactions it resembles methane, ethane and other paraffins.

Ethylene (and other olefines), however, contrast strongly with the almost chemically inert paraffin hydrocarbons in their much greater reactivity due to their ability to form so-called *addition compounds*, as depicted in the following general reaction—



These *addition reactions* are clearly due to the ethylene molecule having two less hydrogen atoms compared with ethane; ethylene is accordingly referred to as an *unsaturated* hydrocarbon. Examples of these addition reactions include—

(*a*) *Reaction with Halogens.* Ethylene combines directly with chlorine at ordinary temperatures to form ethylene dichloride—



(that is, $C_2H_4Cl_2$)

Similar reactions occur with bromine and with iodine. The reaction with bromine is often used as a test for an unsaturated hydrocarbon, and is usually carried out by adding a little bromine water to the gas. The disappearance of the bromine colour on shaking the mixture results from the addition reaction—

$$C_2H_4 + Br_2 \rightarrow \underset{\substack{\text{ethylene}\\\text{dibromide}}}{C_2H_4Br_2}$$

(*b*) *Reaction with Hydrogen Halides.* The following addition reactions

occur most readily with hydrogen iodide and least readily with hydrogen chloride—

$$C_2H_4 + HI \rightarrow \underset{\text{ethyl iodide}}{C_2H_5I}$$

$$C_2H_4 + HBr \rightarrow \underset{\text{ethyl bromide}}{C_2H_5Br}$$

$$C_2H_4 + HCl \rightarrow \underset{\text{ethyl chloride}}{C_2H_5Cl}$$

Note—In the above reactions with the halogens, the order of decreasing reactivity is chlorine, bromine and iodine, that is, the reverse of the reactivity with the halogen hydrides.

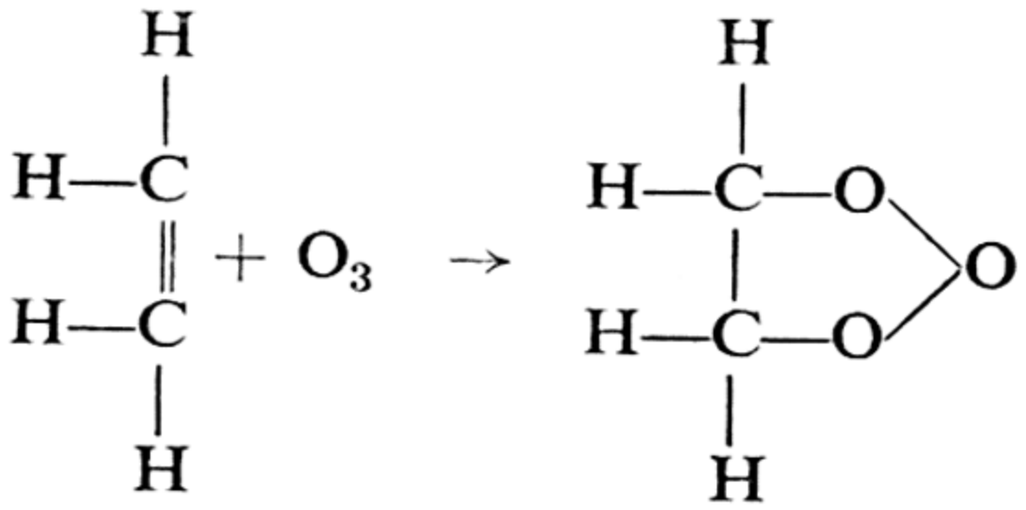
(*c*) *Reaction with Hydrogen.* If a mixture of ethylene and hydrogen is passed over a finely divided nickel catalyst at about 150°C, or is bubbled through a colloidal suspension of platinum at ordinary temperatures, addition occurs to form ethane—

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

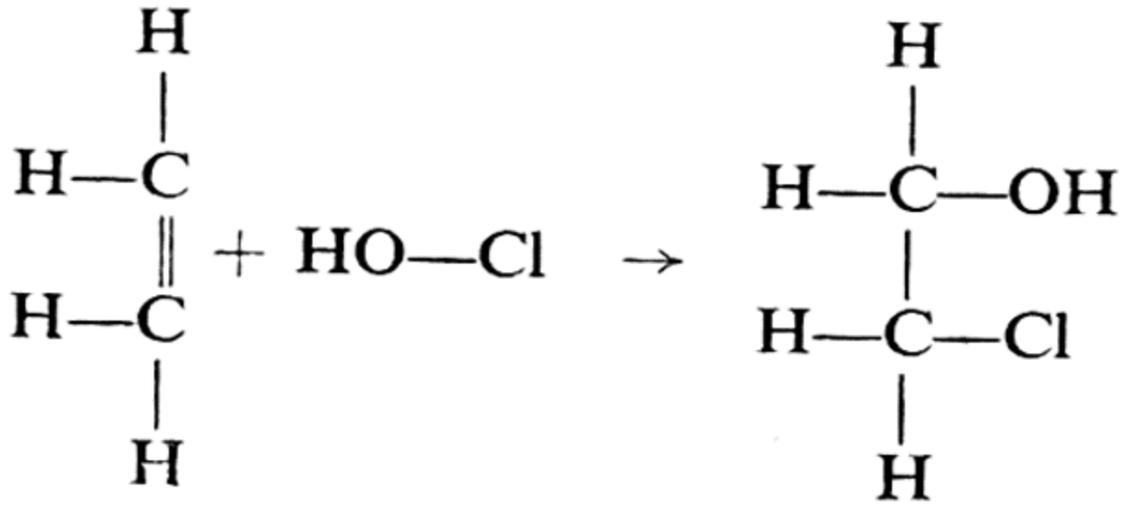
(*d*) *Reaction with Sulphuric Acid.* Fuming sulphuric acid will absorb ethylene very rapidly at ordinary temperatures to form ethyl hydrogen sulphate, and this reaction is used industrially to remove unsaturated hydrocarbons from admixture with saturated hydrocarbons, as for example in oil refining. The reaction with concentrated sulphuric acid occurs only slowly in the cold, but proceeds readily at about 100°C—

$$C_2H_4 + H_2SO_4 \rightarrow \begin{matrix} C_2H_5 \\ H \end{matrix}\!\!\rangle SO_4 \text{ (or, } EtHSO_4)$$

(*e*) *Reaction with Ozone and also with Hypochlorous Acid*

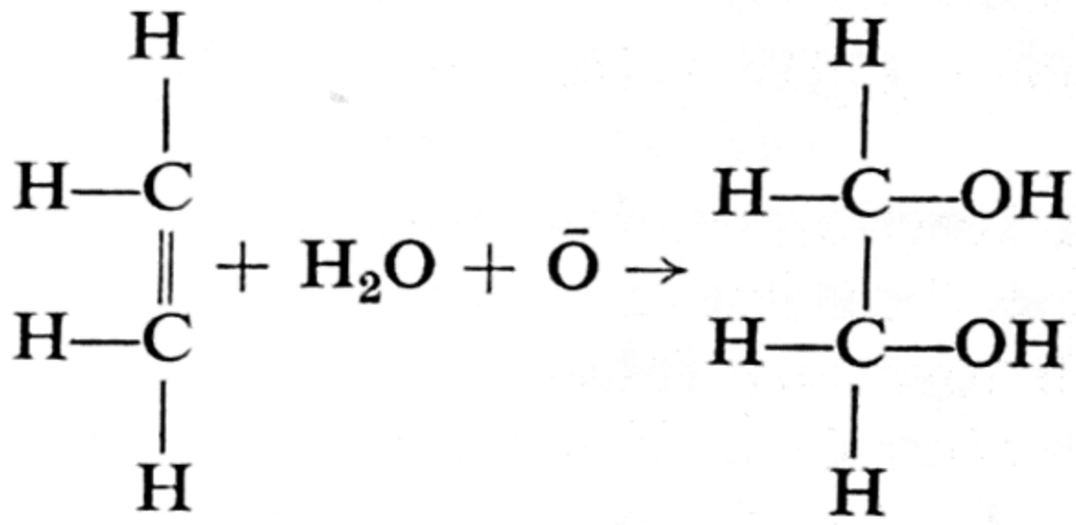


ethylene ozonide,
but see p. 728



ethylene chlorhydrin

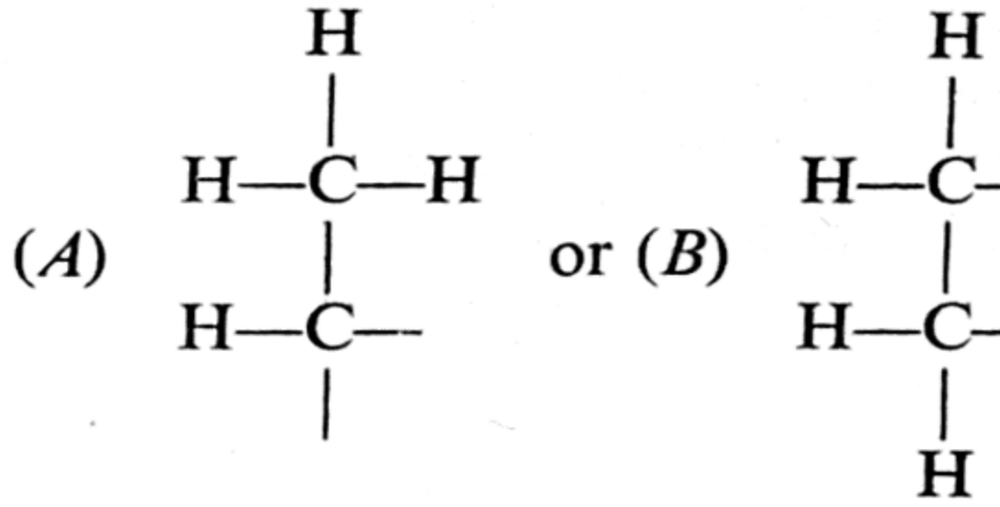
Ethylene is easily oxidized. If 1–2 ml of a very dilute solution of potassium permanganate be added to a gas jar of ethylene and shaken, the purple permanganate colour is replaced by the green colour of potassium manganate (K_2MnO_4), and ultimately by a brown precipitate of manganese dioxide. The ethylene is simultaneously oxidized to ethylene glycol—



ethylene glycol

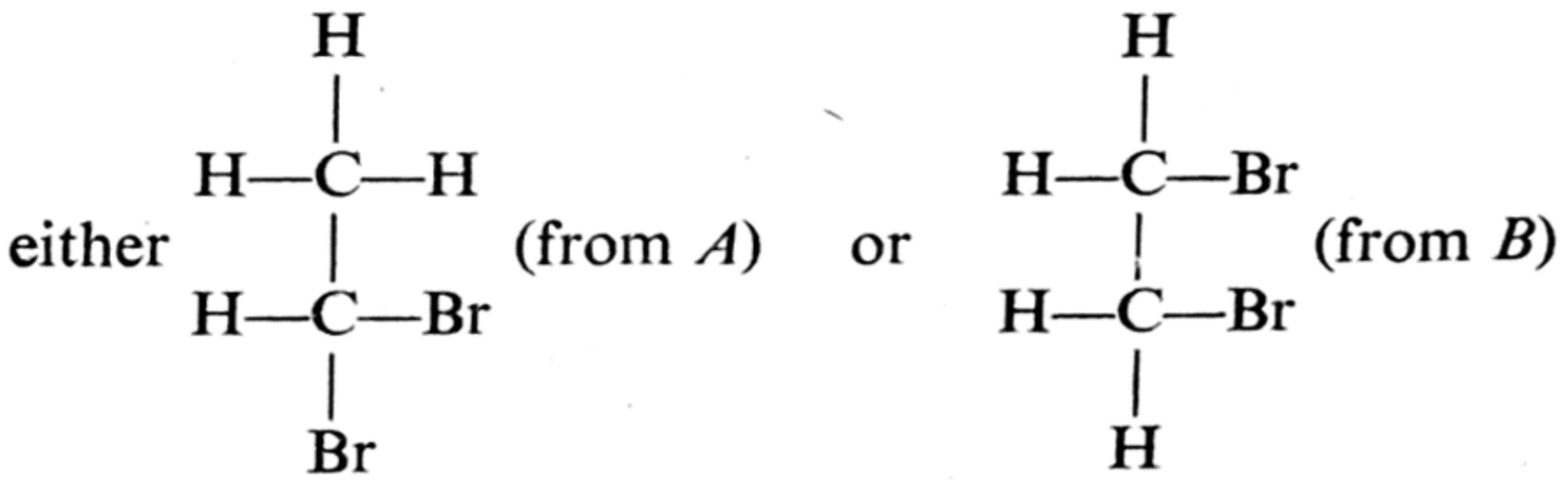
If acidified permanganate be used, the colour changes observed are from purple to colourless, and further oxidation of the ethylene glycol occurs.

Structural Formula of Ethylene. The addition reactions of ethylene show that the molecule is not saturated, and suggests that its structural formula is *either*

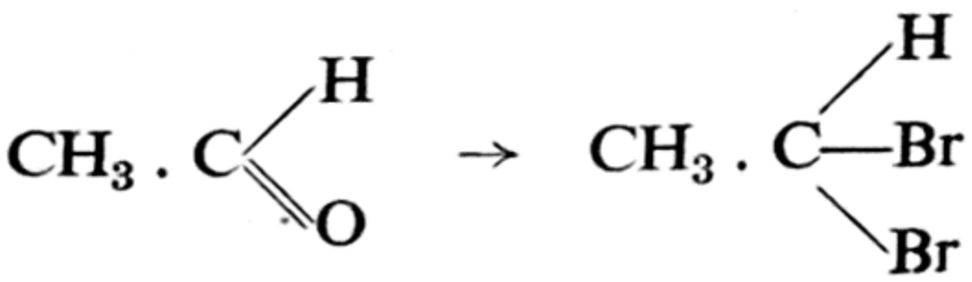


That the first of these two formulae is incorrect is shown by the following arguments—

(*a*) Ethylene forms an addition compound with bromine having the formula $C_2H_4Br_2$, the structural formula of which would be—



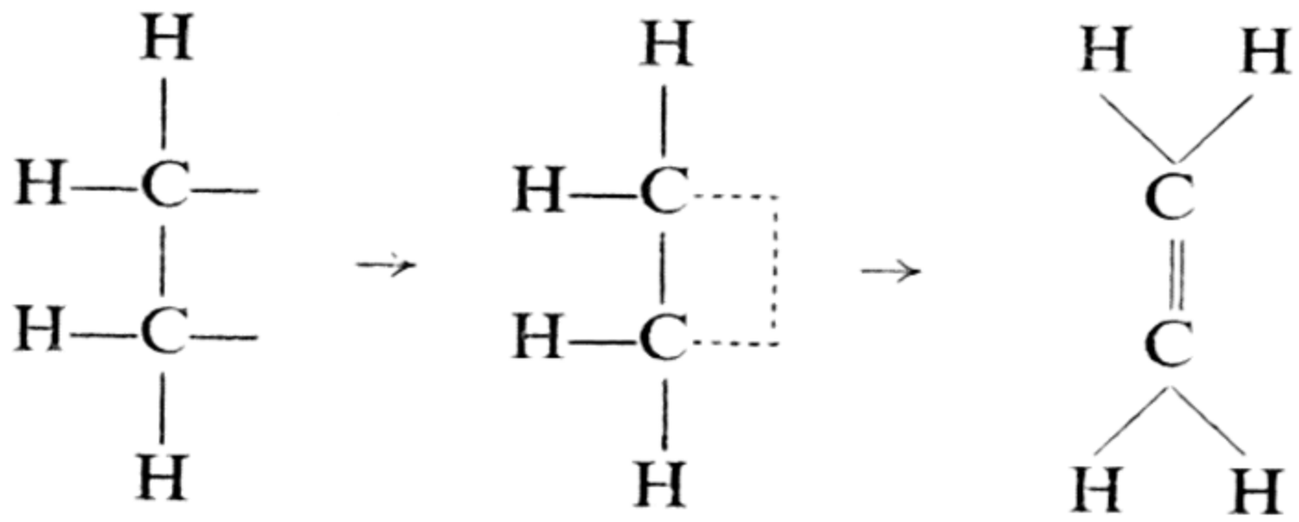
(*b*) A compound having the first of these two structures may be prepared by the action of phosphorus and bromine on acetaldehyde—



This compound is different, however, from that produced by the reaction of bromine with ethylene.

(*c*) This suggests that the dibromo-derivative of ethylene has the second formula, $CH_2Br \cdot CH_2Br$, and therefore that ethylene has the structure (*B*) above.

The formula (*B*), however, cannot be completely correct since it involves the presence of free valency bonds on the carbon atoms. In this respect it would resemble the methyl radical, CH_3-, and like this and other radicals would presumably be incapable of a separate existence. It is suggested, therefore, since ethylene definitely does exist, that the two free valency bonds on adjacent carbon atoms mutually saturate each other to form an additional bond between the two carbon atoms, thus—



ethylene

Ethylene is thus regarded as possessing a double bond, with each carbon showing its normal four-covalency. The ability of adjacent carbon atoms to form an additional bond in this way is supported by the non-existence of a compound CH_2. Ethylene is in fact the first member of the olefine series.

FIG. 257. Structure of Ethylene

It should be well understood that the "double bond" is simply a convention for bringing the clearly unsaturated valency bond structure of ethylene into line with the rule that compounds having free valency bonds cannot exist as stable compounds. The double bond, therefore, should not be taken to indicate a stronger force between the two carbon atoms, but instead it should be regarded as the point of weakness in the molecule at which chemical reaction takes place.

Baeyer explained this inherent reactivity of the double bond in terms of the strain which would be set up by linking two carbon atoms together by more than one bond. When two carbon atoms are linked together by single bonds, as in ethane, no distortion of the carbon valency bonds from their tetrahedral arrangement occurs, so that the resulting molecule is "free from strain." When two carbon atoms become doubly linked together, as in ethylene, however, the two pairs of valency bonds undergoing mutual saturation must be distorted from their tetrahedral arrangement. The strain so introduced leads to instability.

Furthermore, the two carbon atoms in this latter case will be rather closer together than they would be if only singly linked (1·34 cf. 1·54 Angstrom units). This closer approach of the carbon atoms increases the internal energy and hence reactivity of the molecule.

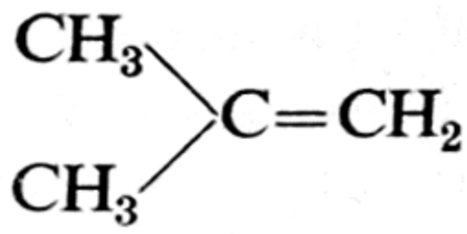
The Olefine Series

The general formula for the members of this series is C_nH_{2n}, with ethylene as the first member. Examples include—

$CH_3—CH=CH_2$ propylene

$CH_3—CH_2—CH=CH_2$ normal-butylene

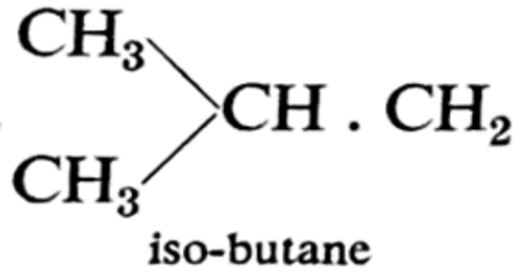
and



iso-butylene

In addition to the chain isomerism encountered with the paraffins, the olefines show additional isomerism due to variation in the position of the double bond. Thus there are three isomers of butylene compared with only two of butane—

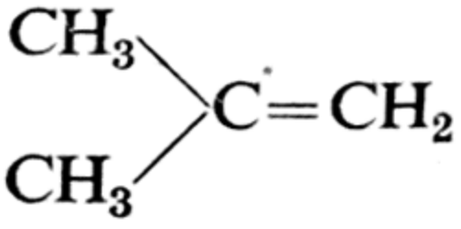
$CH_3 . CH_2 . CH_2 . CH_3$
n-butane



iso-butane

$CH_3 . CH_2 . CH=CH_2$
normal-butylene
(*n*-butylene)

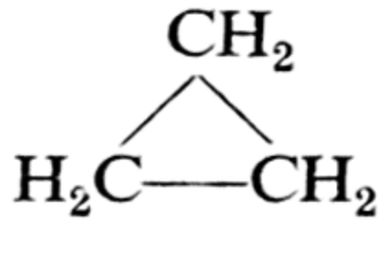
$CH_3 . CH=CH . CH_3$
symmetrical butylene
(dimethyl ethylene)



iso-butylene

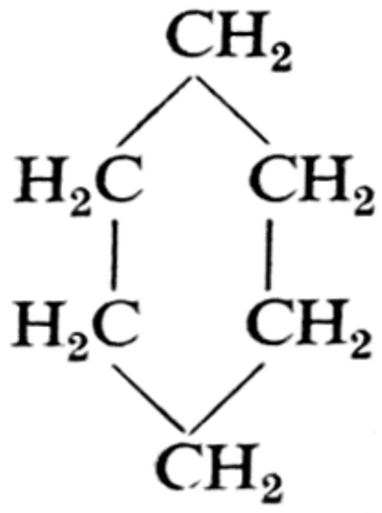
It should be noted also that the *polymethylene* compounds or cyclo-paraffins also have the general formula C_nH_{2n}, and are therefore isomeric with the corresponding ethylenes. Examples of these hydrocarbons include—

Cyclo-propane or Trimethylene



(that is, C_3H_6)

Cyclo-hexane or Hexamethylene



(that is, C_6H_{12})

The reactions of the olefines are those already described in connexion with ethylene, the first member of the series.

General Methods of Preparation. The methods described in connexion with ethylene may also be used to prepare other olefines. The most general method, only briefly described in the case of ethylene because of the poor yield obtained of this gas, is to heat the alkyl iodide with an alcoholic solution of potassium hydroxide. The reaction may be carried out by slowly running the alkyl iodide from a tap-funnel into the heated solution of potassium hydroxide in alcohol as shown in the diagram below. The

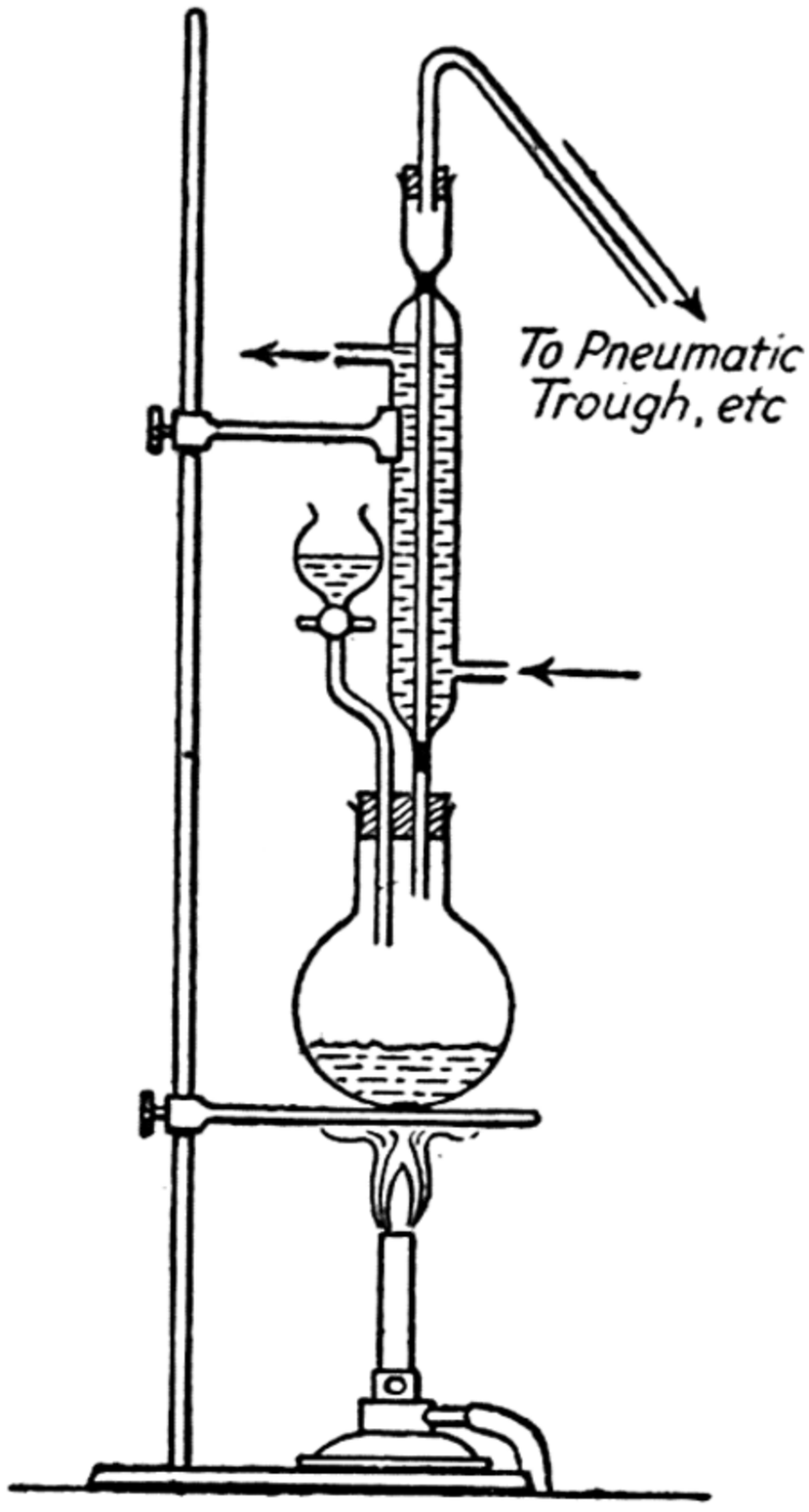


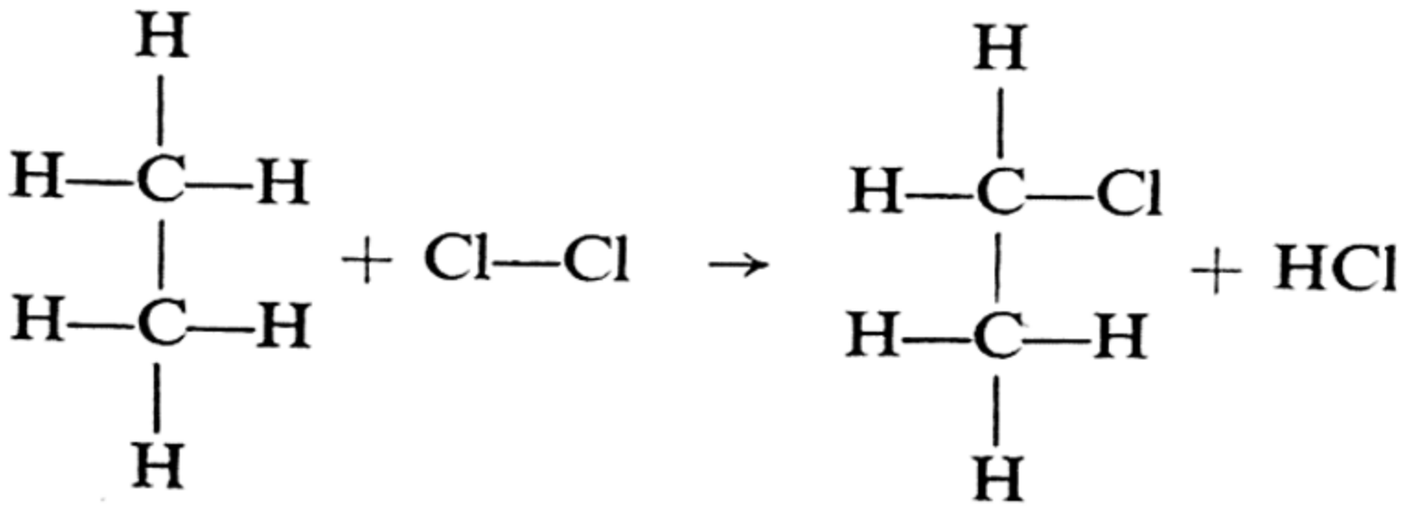
FIG. 258. Preparation of Olefines from Alkyl Iodines

reflux condenser serves to return any alkyl iodide and alcohol vapour to the reaction vessel.

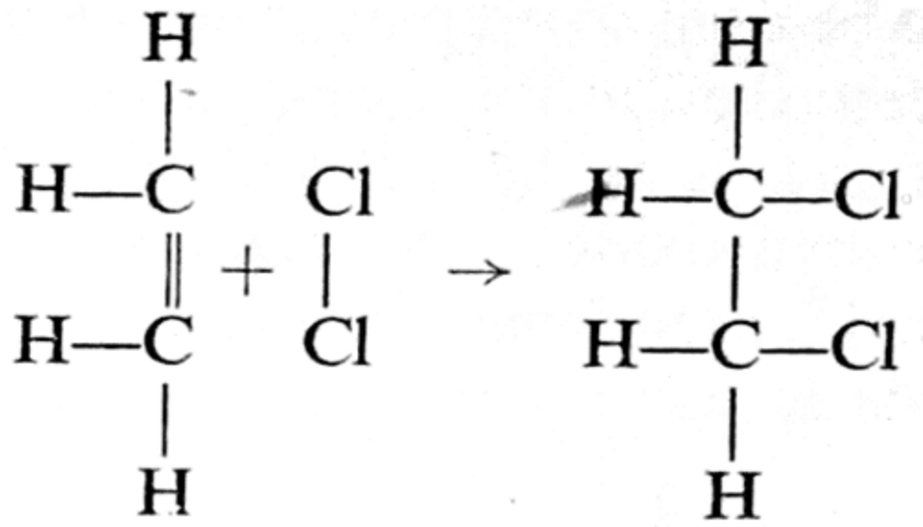
$$C_nH_{2n+1}I + KOH \rightarrow C_nH_{2n} + KI + H_2O$$

Essential Difference in Reaction between Paraffins and Olefines

Paraffins are *saturated* hydrocarbons and form *substitution* compounds



Olefines are *unsaturated* hydrocarbons and form *addition* compounds



ethylene dichloride

THE ACETYLENES

The acetylene hydrocarbons are characterized by the presence in their molecules of a so-called *triple-bond.* For example, the simplest and also most important member of the series, acetylene, has the molecular formula

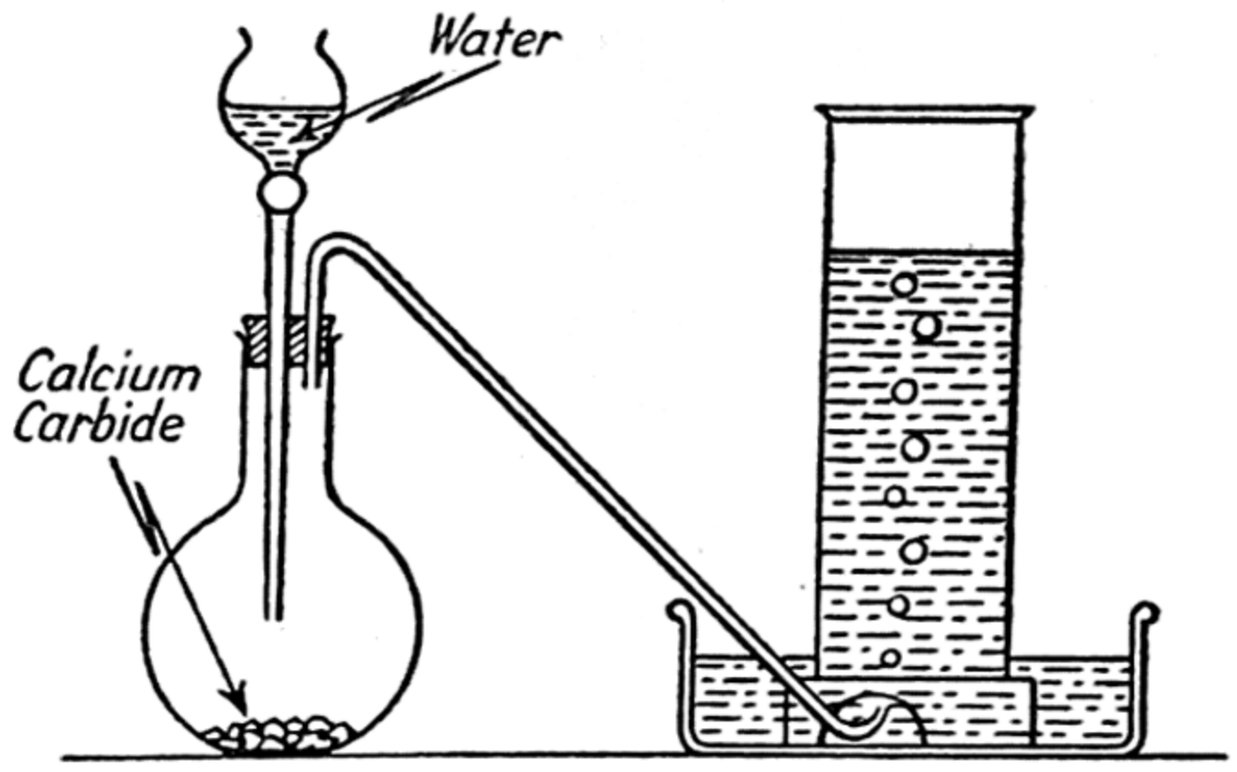
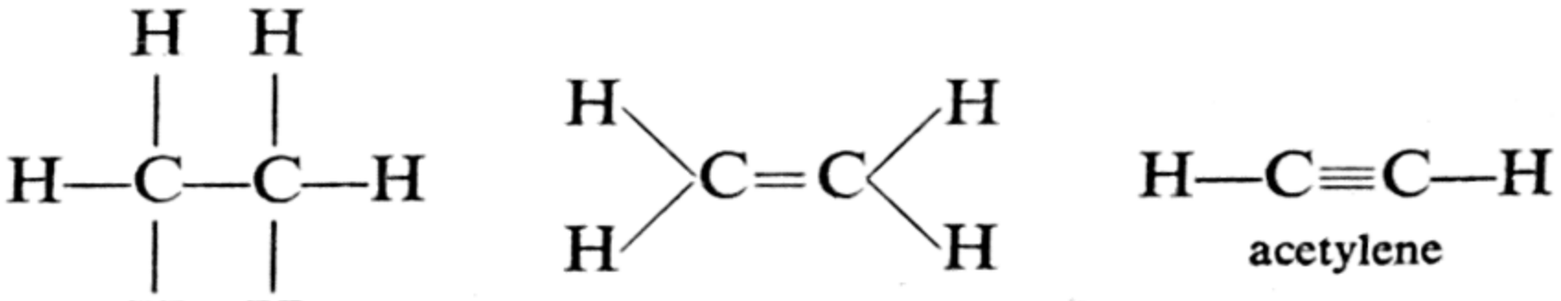


FIG. 259. Preparation of Acetylene from Calcium Carbide

C_2H_2, and therefore contains two hydrogen atoms less than ethylene and four less than ethane—



ethane ethylene acetylene

Homologues of acetylene include propyline (or, methyl acetylene), $CH_3 . C{\equiv}CH$, butyline (or, ethyl acetylene) $CH_3 . CH_2{-}C{\equiv}CH$, and so on.

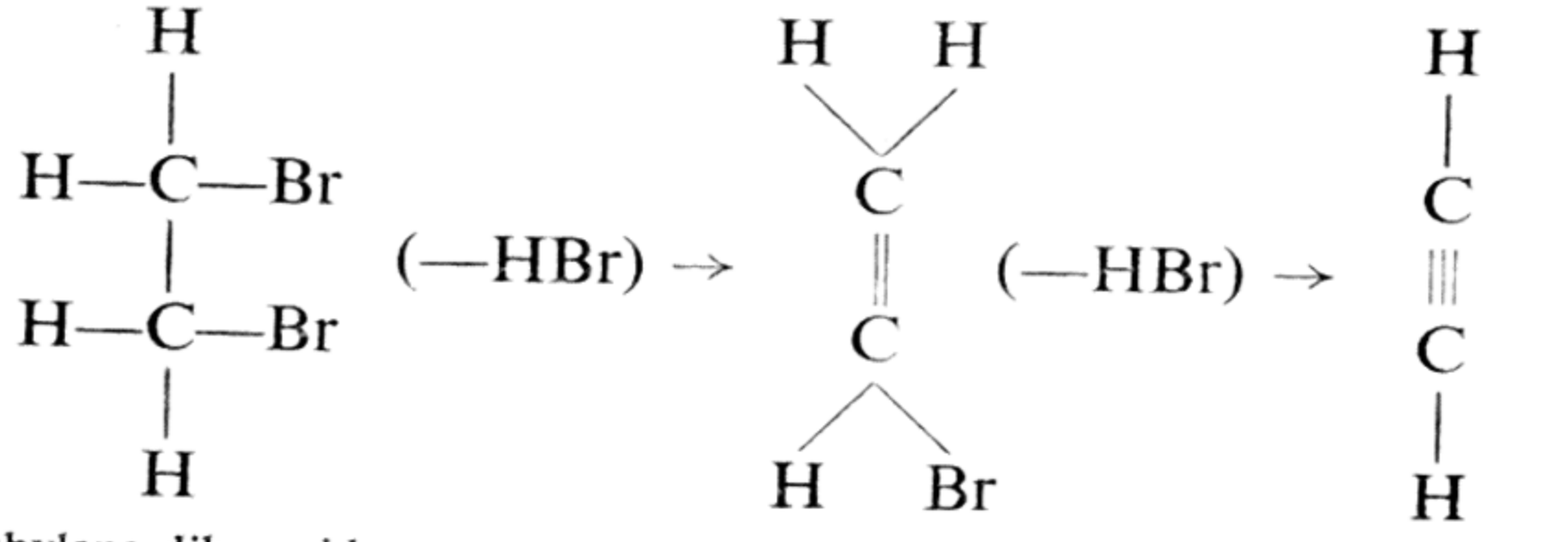
Preparation of Acetylene. The most important laboratory and also industrial method is by the action of water on calcium carbide—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

Impurities, such as calcium phosphide, sulphide and nitride, in the calcium carbide may result in small quantities of phosphine, sulphuretted hydrogen

and ammonia being liberated at the same time, and these give the acetylene an objectionable smell. Most of these impurities may be removed by bubbling the gas through a solution of copper sulphate before collecting the acetylene.

The general method for preparing acetylenes is by heating dihalogen compounds, such as ethylene dibromide, with an alcoholic solution of sodium or potassium hydroxide. The reaction occurs in two distinct stages, corresponding to the removal of two separate molecules of hydrogen bromide. The product is relatively pure.



ethylene dibromide — vinyl bromide — acetylene

This reaction with *alcoholic* potassium hydroxide should be compared with that of *aqueous* potassium hydroxide which merely hydrolyzes the ethylene dibromide to form ethylene glycol—

$$C_2H_4Br_2 + 2KOH\ (alcoholic) = C_2H_2 + 2KBr + 2H_2O$$
$$C_2H_4Br_2 + 2KOH\ (aqueous) = C_2H_4(OH)_2 + 2KBr$$

A modification of the alcoholic potassium hydroxide method which is particularly suitable for preparing acetylene is to pass the ethylene dibromide vapour over heated soda-lime contained in a hard-glass tube (*see* p. 870 for diagram of apparatus).

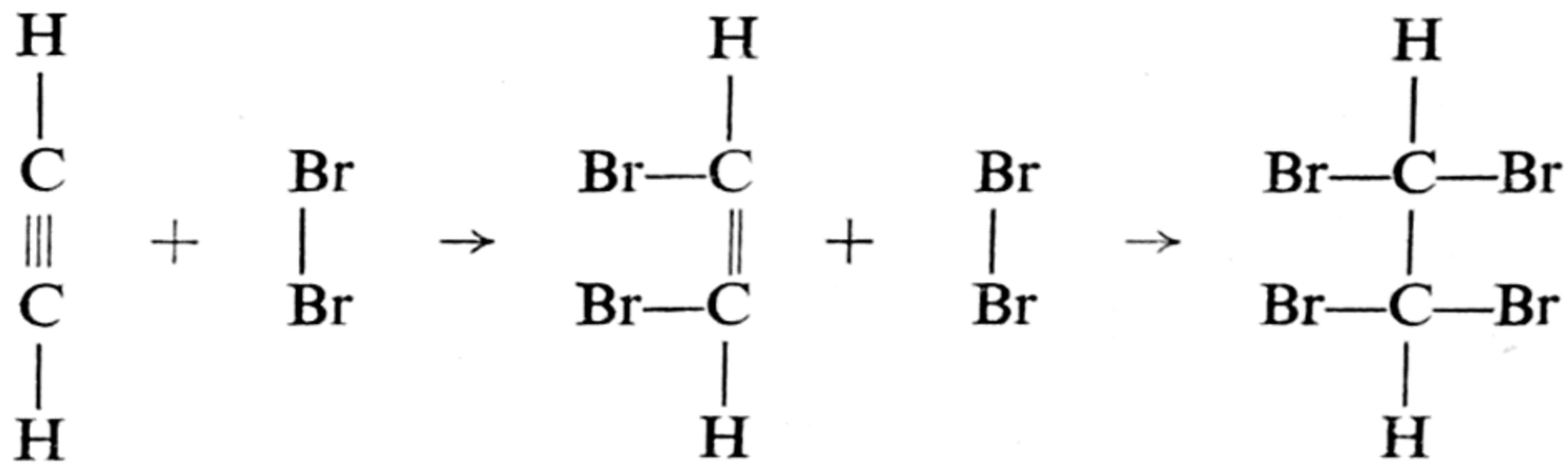
Properties. Acetylene is a colourless gas, almost odourless when pure, but as normally prepared it has a pronounced and unpleasant odour. It is slightly soluble in water but is much more soluble in organic solvents such as acetone and hydrocarbons. If acetylene is required in large quantities it is usually obtained from steel cylinders which contain a solution of acetylene under pressure in acetone, the latter being absorbed in some porous material such as *kieselguhr*. Any acetone vapour carried over with the acetylene may be removed by bubbling through water. The storage of acetylene by itself under pressure is dangerous since explosions are liable to occur.

Acetylene burns in air with a very smoky flame due to incomplete oxidation which results in deposition of carbon. If, however, acetylene is allowed to burn at a small jet in a plentiful supply of air or oxygen complete oxidation occurs to form a very hot bright flame. In the familiar acetylene lamp, two very fine jets of acetylene are directed towards one another to produce a very thin sheet of flame with maximum surface exposed to the

air or oxygen. The very high temperature (greater than 3000°C) produced by the complete combustion of acetylene in oxygen is used, in the oxy-acetylene blow-pipe, for such purposes as the welding and cutting of metals. In the former case the proportions of oxygen and acetylene are controlled so that carbon monoxide and steam are formed, thus avoiding oxidation of the metal. In the latter case, excess of oxygen is used, the cutting action then resulting from burning of the metal.

Like the other gaseous hydrocarbons, mixtures of acetylene and air or oxygen are liable to explode violently when ignited. For this reason, it is important when preparing these gases (e.g. methane, ethylene, acetylene) in the laboratory to allow the reaction to proceed for some little time before collecting the gases.

The doubly unsaturated nature of acetylene is revealed by its addition reactions which are similar to those of ethylene but involve two molecules of the reagent instead of the one required by ethylene—

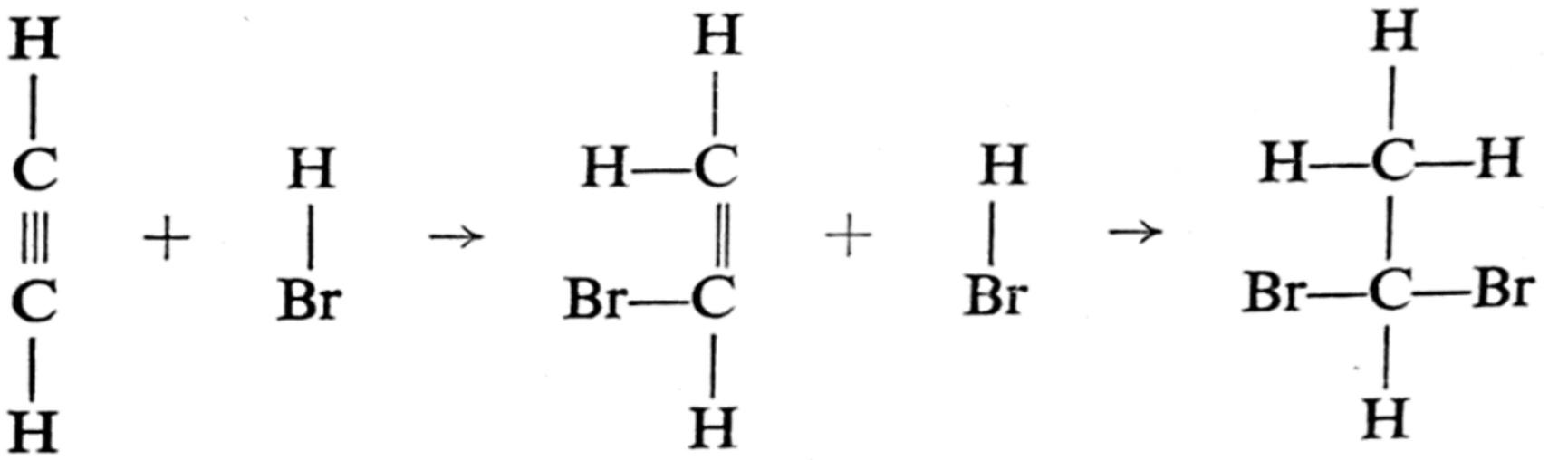


acetylene — acetylene dibromide — acetylene tetrabromide

The reaction of bromine (and bromine-water) with acetylene occurs very much less readily than with ethylene. This slower reaction is also in marked contrast to the action of chlorine-water with acetylene which occurs with explosive violence. Acetylene, therefore, must not be tested with chlorine or chlorine-water unless special safety precautions are observed.

$$C_2H_2 + Cl_2 \rightarrow 2C + 2HCl$$

The addition reactions of acetylene with the hydrogen halides (HCl, etc.) should be noted because of the formation of unsymmetrical di-halides in which both the halogens are on the same carbon atom—



acetylene — vinyl bromide — ethylidene dibromide

The alternative reaction in which the second molecules of HBr adds on to

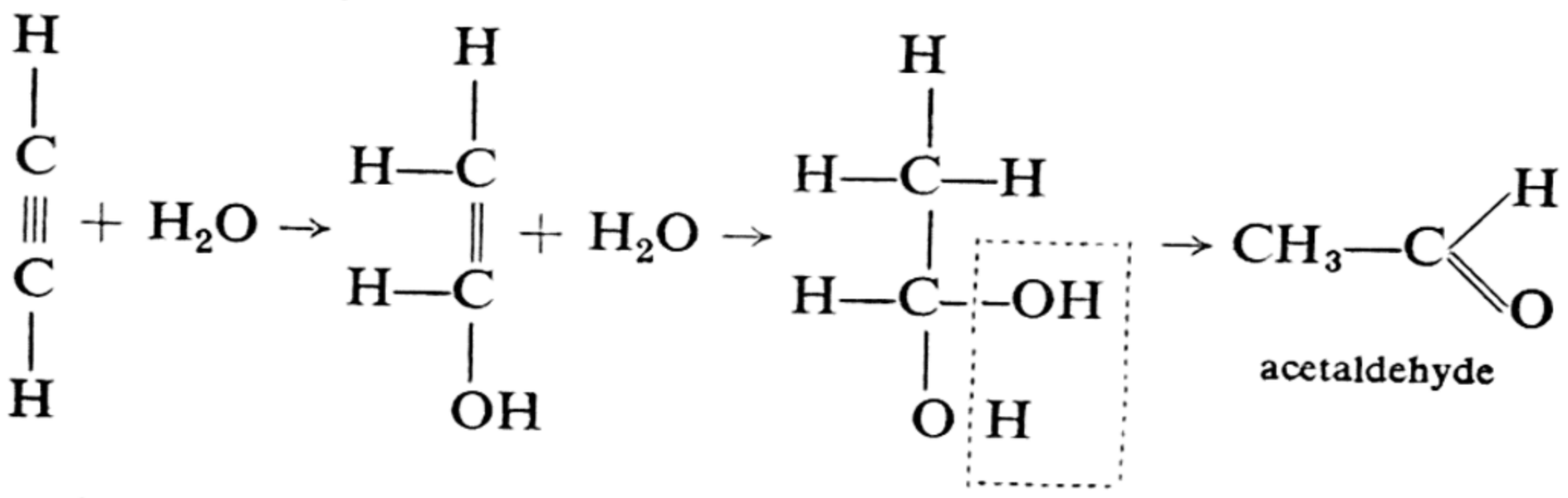
vinyl bromide to give symmetrical ethylene dibromide, $CH_2Br—CH_2Br$, does not occur. The rule governing this type of addition is known as *Markownikoff's Rule*. This states simply, to borrow a phrase from the Bible, that "to him that hath shall be given." Thus, in the above reaction the carbon atom with the most hydrogen is the carbon atom which receives the additional hydrogen atom of the hydrogen bromide. Note, that the univalent radical $CH_2=CH—$ is known as *vinyl*, the compound, $CH_2=CHBr$ being known therefore as *vinyl bromide*.

Addition of hydrogen to form first ethylene and then ethane occurs when a mixture of acetylene and hydrogen is passed over a finely divided nickel catalyst at about 150°C (Sabatier and Senderens reaction), or through a colloidal solution of platinum at ordinary temperatures.

$$C_2H_2 + H_2 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_6$$

Oxidation of acetylene occurs readily. Thus with alkaline potassium permanganate, a brown precipitate of manganese dioxide quickly forms with a transient formation of the green potassium manganate. With acidified potassium permanganate, the colour change is from purple to colourless.

The reaction of acetylene with sulphuric acid is very important industrially. When acetylene is passed into a warm solution of sulphuric acid containing a small amount of a mercuric salt as catalyst, the very important compound acetaldehyde is formed.



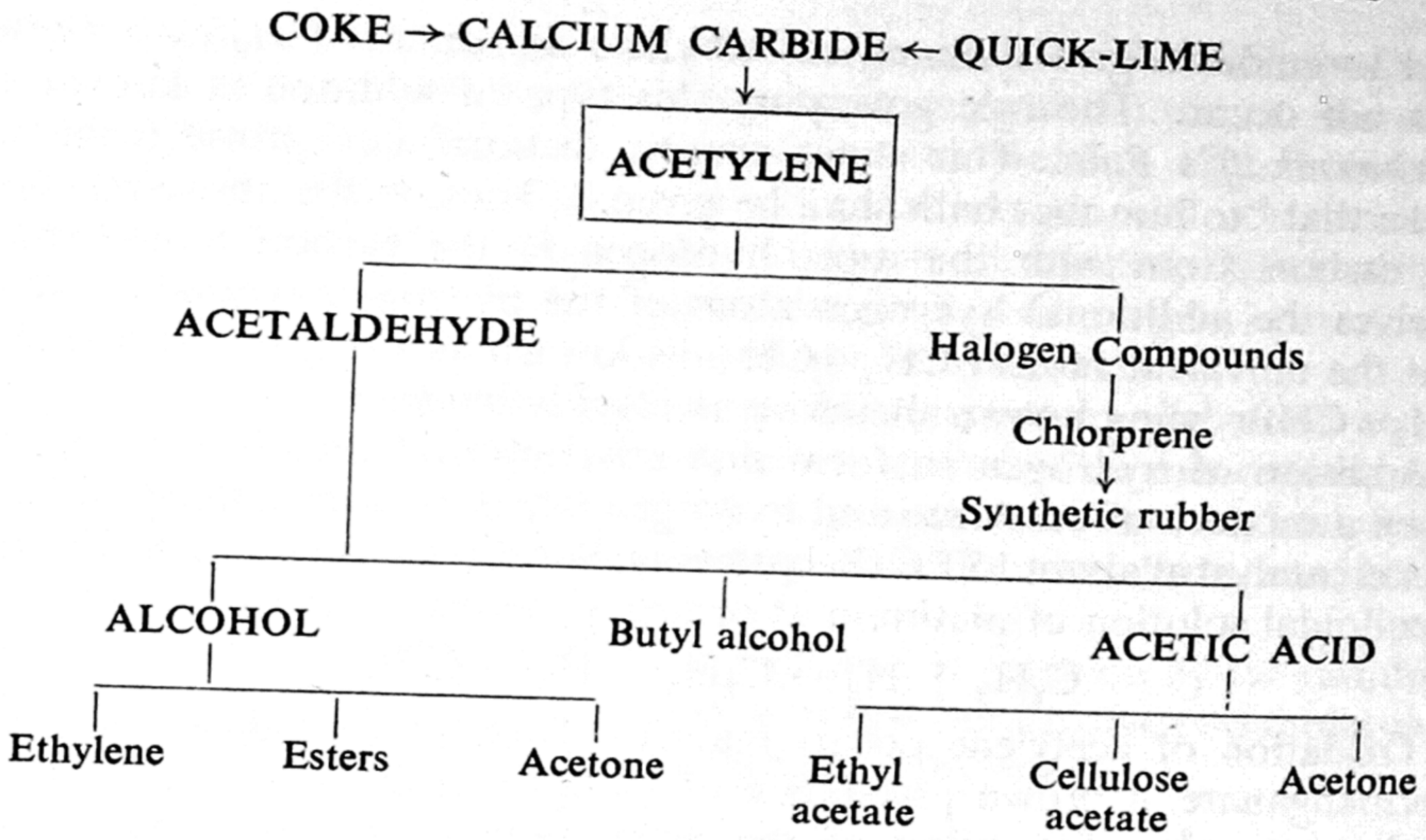
This reaction, in conjunction with the manufacture of acetylene from calcium carbide, shows how the vast deposits of carbon (coal) may be used to synthesize a host of important compounds and materials, some of which are shown in the table on p. 882.

Metallic Compounds. Acetylene (and other homologues possessing the group, $—C\equiv CH$), form metallic derivatives known as acetylides. The acetylides of the alkali and alkaline earth metals are comparatively stable solids and are formed by passing acetylene over the heated metal—

$$C_2H_2 + 2Na \rightarrow H_2 + \underset{\text{sodium acetylide}}{Na_2C_2}$$

With water these acetylides react to liberate acetylene—

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

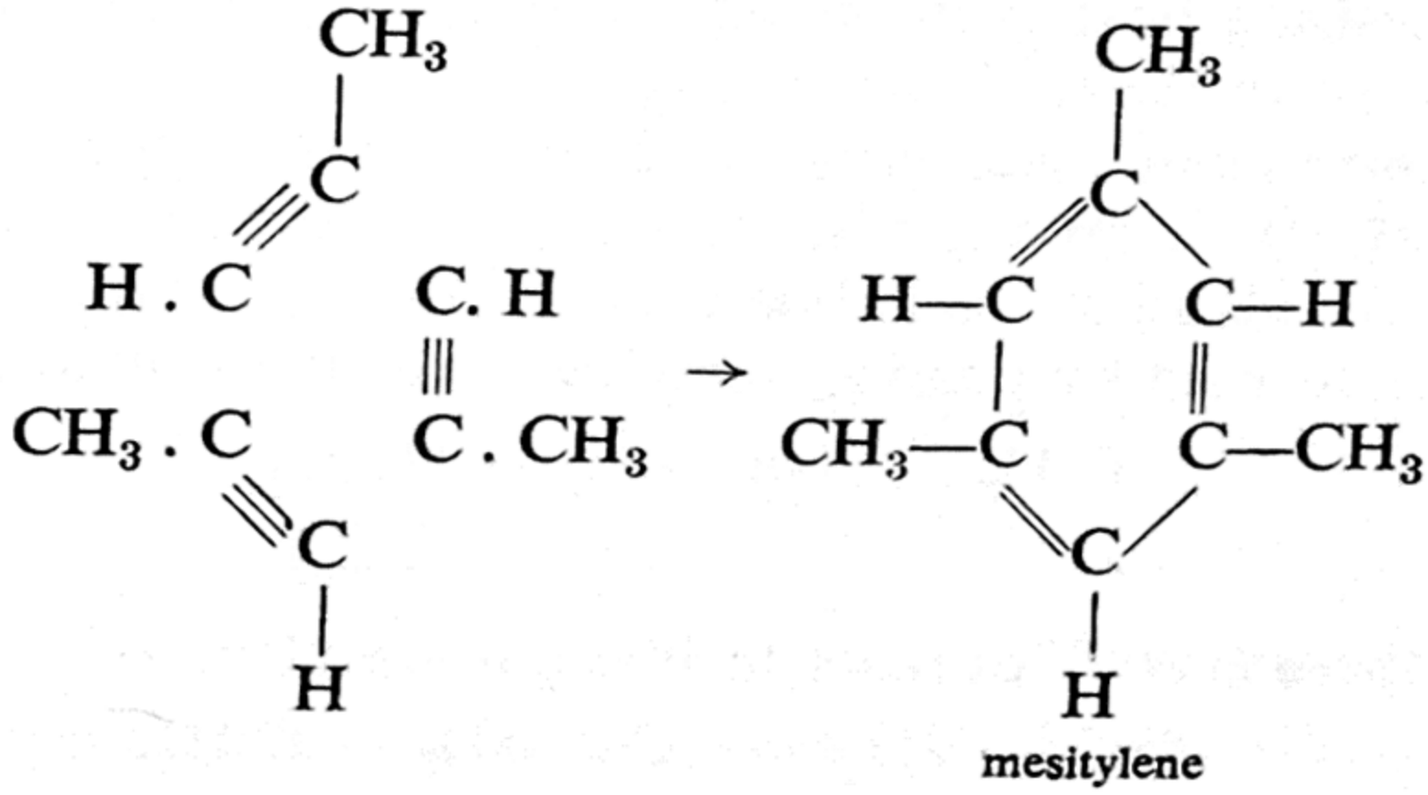


The acetylides of the baser metals (copper and silver, for example), however, are explosive compounds when dry, and are not decomposed by water. With dilute acids, however, they react to liberate acetylene, a method which is sometimes used to prepare small quantities of the pure gas. Silver acetylide, Ag_2C_2, is formed as a white insoluble powder when acetylene is passed into an ammoniacal solution of silver nitrate. Similarly, when acetylene is passed into an ammoniacal solution of cuprous chloride, a red precipitate of cuprous acetylide, Cu_2C_2, is formed. These acetylides may be handled with safety when wet, but on no account should they be dried.

Polymerization. When acetylene is passed through a tube heated to dull redness, a small quantity of benzene is formed—

$$3C_2H_2 \rightarrow \underset{\text{benzene}}{C_6H_6}$$

This is an example of a *polymerization* reaction. Allylene similarly polymerizes to form mesitylene—



mesitylene

Note that polymerization results in the formation of a *new compound* with the same general formula as the monomer, as expressed in the equation—

$$Monomer,\ n(A) \rightarrow Polymer,\ (A)_n$$

Formula of Acetylene. The arguments put forward for the double bond in ethylene apply also to the triple bond in acetylene. On Baeyer's Strain theory, the very great reactivity of acetylene results from—

(*a*) The strain involved in forming a triple bond between three pairs of tetrahedrally disposed carbon valency bonds, and

(*b*) the increased internal energy which results from the two carbon atoms being closer together than in ethylene and in ethane (1·20 Å, cf. 1·34 Å in ethylene and 1·54 Å in ethane).

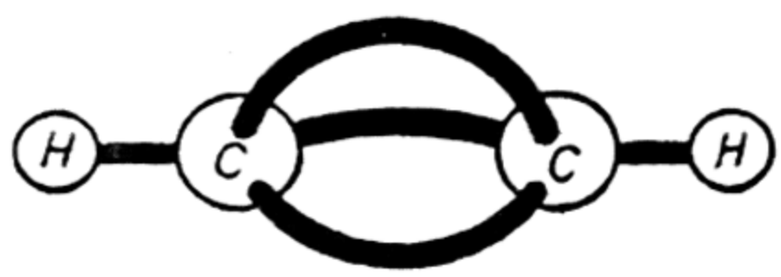


FIG. 260. Structure of Acetylene

Acetylene Series

The members of this series have the general formula C_nH_{2n-2}, but the names are not systematic as in the case of the paraffin and olefine series.

Paraffins	*Olefines*	*Acetylenes*
Methane, CH_4	—	—
Ethane, C_2H_6	Ethylene, C_2H_4	Acetylene, C_2H_2
Propane, C_3H_8	Propylene, C_3H_6	Allylene, C_3H_4
Butane, C_4H_{10}	Butylene, C_4H_8	Crotonylene, C_4H_6

Isomerism may occur as in the ethylene series due to (*a*) chain isomerism and (*b*) position of the triple bond isomerism. The resulting compounds are also isomeric with the corresponding di-olefines (that is, compounds having two double bonds), and in certain cases with unsaturated ring compounds. Thus compounds having the formula C_5H_8 include—

Acetylenes

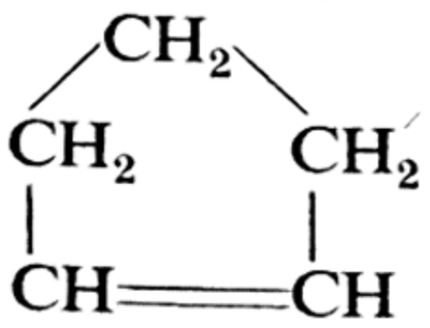
$$CH_3—CH_2—CH_2—C{\equiv}CH;\quad CH_3—CH_2—C{\equiv}C—CH_3;$$

$$\begin{matrix} CH_3 \\ \diagdown \\ \quad CH—C{\equiv}CH \\ \diagup \\ CH_3 \end{matrix}$$

Di-olefines

$$CH_3—CH{=}CH—CH{=}CH_2;$$

Unsaturated Ring Compounds



CHAPTER 29

ALKYL HALIDES

THE first of the homologous series to be studied after the paraffins, the olefines and the acetylenes, is that of the *alkyl halides*. These may be regarded as paraffins in which one of the hydrogen atoms has been replaced by a halogen atom; for example, methyl chloride, CH_3Cl. The alkyl halides are particularly important because of the ease with which the halogen atom can be replaced by other radicals to form a large number of different organic compounds. Examples of these reactions are given later in the present chapter on p. 886.

There are four homologous series of alkyl halides, each having the general formula, $C_nH_{2n+1}X$, in which "X" may be F, Cl, Br or I. Little is known about the alkyl fluorides, but the chlorides, bromides and iodides are well known to all organic chemists. In the following table are given the boiling points of the earlier members of each series, and also their state (that is, whether gas, liquid, or solid) at ordinary temperatures.

TABLE 115

Boiling Points of Simple Alkyl Halides

Alkyl-	Chloride		Bromide		Iodide	
	Boiling Point	State	Boiling Point	State	Boiling Point	State
	(°C)		(°C)		(°C)	
Methyl- .	− 23·7	Gas	+ 4·5	Gas	+ 45	Liquid
Ethyl- .	+ 12·2	Gas	38·4	Liquid	72·8	Liquid
n-Propyl- .	46·5	Liquid	71·0	Liquid	102·5	Liquid
iso-Propyl-	36·5	Liquid	60·0	Liquid	89·5	Liquid

In the general methods for preparing these alkyl halides described below, the examples chosen are liquid alkyl halides because of their greater ease of collection compared with gases and their more frequent use in preparing other organic compounds.

General Methods of Preparation

From Paraffins. It has been stated, in connexion with the reactions of the paraffins, that direct reaction occurs with the halogens to form various

substitution products. As a method for preparing particular alkyl halides, however, the method is practically useless, since the reaction cannot be controlled and results in a complex mixture of various mono-, di-, tri-, etc., halogen substitution products.

From Alcohols. Two general methods are available—

(*a*) The reaction—

$$EtOH + HBr \rightleftharpoons EtBr + H_2O$$

is reversible. The presence of a dehydrating agent is therefore necessary to remove the water product and so minimize the back reaction. Like most organic reactions, the reaction also occurs comparatively slowly at ordinary temperatures, but the rate may be increased by increasing the

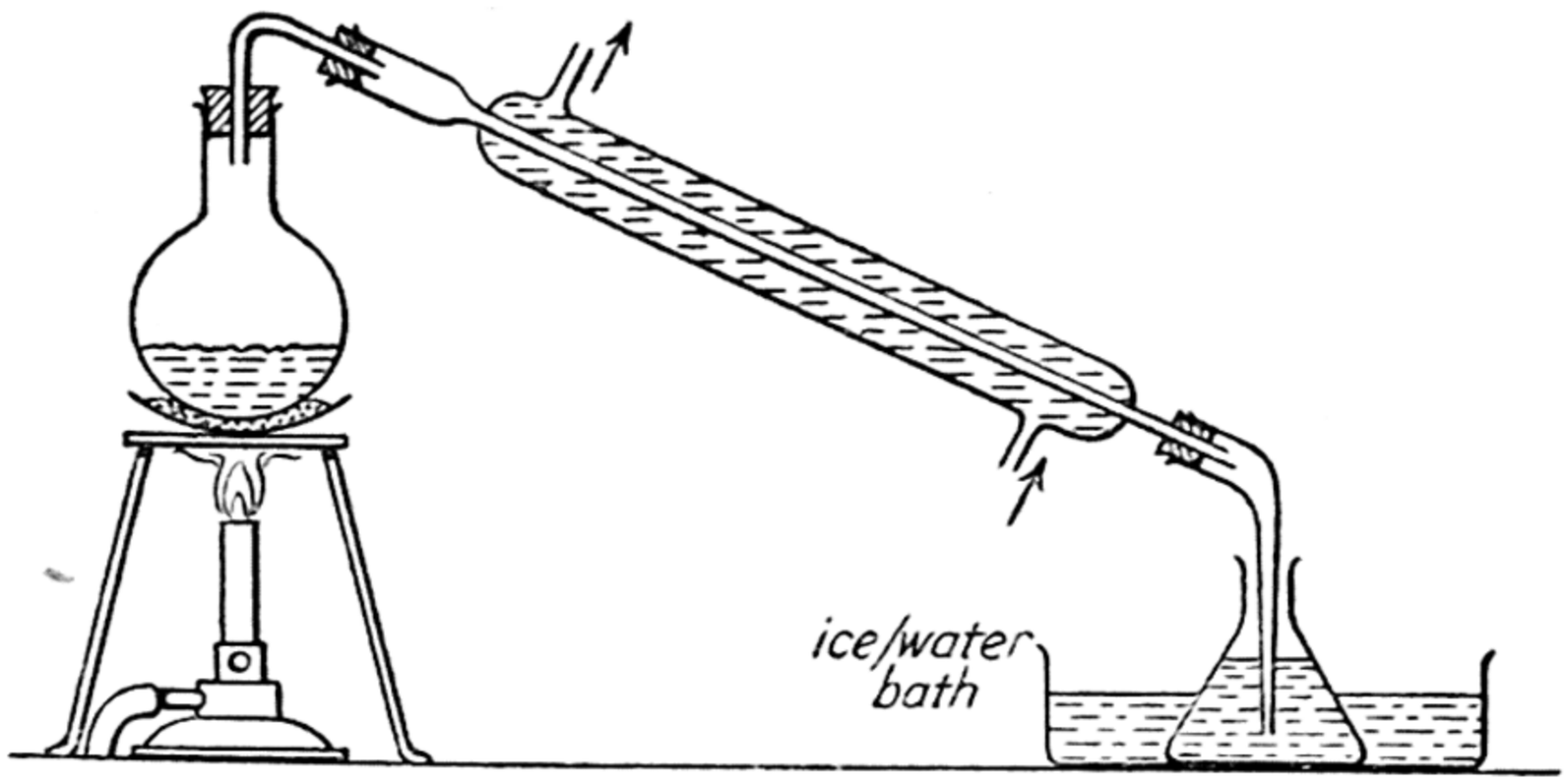


FIG. 261. Preparation of Ethyl Bromide

temperature. The reaction is therefore carried out under anhydrous conditions in the hot in the presence of a dehydrating agent.

(i) In Groves process the reaction is carried out by passing the dry hydrogen halide gas (e.g. HBr) into a heated mixture of absolute alcohol and anhydrous zinc chloride.

(ii) A modification is to heat the absolute alcohol with a mixture of concentrated sulphuric acid (in excess) and potassium bromide (or other halide). The sulphuric acid serves both to liberate the anhydrous hydrogen bromide and also to remove the water liberated in the reaction. The sulphuric acid is added slowly to the alcohol in the flask (with the usual precautions), and then after adding some coarsely ground potassium bromide the apparatus is assembled as in the diagram above. The ethyl bromide collects as heavy oily drops under water in the receiver. The ethyl bromide is then separated, any acid neutralized by shaking with sodium carbonate solution, and finally, after separating the latter and washing with water, it is dried with anhydrous calcium chloride.

(*b*) A convenient method, particularly suited for the preparation of the alkyl bromides and iodides, is to heat the alcohol with the phosphorus

halide. In the case of the chlorides, phosphorus penta- or tri-chlorides may be used, but for the bromides or iodides, the phosphorus halide is prepared in situ by adding bromine or iodine to a mixture of alcohol and red phosphorus.

$$R{-}OH + PCl_5 = RCl + POCl_3 + HCl$$

$$\left.\begin{matrix} R{-}OH \\ R{-}OH \\ R{-}OH \end{matrix}\right\} + \left\{\begin{matrix} Br \\ Br \\ Br \end{matrix}\right. = 3RBr + H_3PO_3$$

A little used method is the addition of the hydrogen halide to an olefine—

$$C_2H_4 + HI = C_2H_5I$$

Properties. The alkyl halides are usually colourless liquids, insoluble in water but very soluble in organic solvents. The lower members are either gases (e.g. CH_3Cl) or liquids (e.g. CH_3I), but the melting points and boiling points increase as in other homologous series with increase in molecular weight. In general, the chlorides have the lowest melting points and boiling points, the bromides about 25° higher and the iodides about 40—50° higher again.

Chemically, the alkyl halides are remarkable for the ease with which the halogen atom may be replaced by other substituent groups. This reactivity makes the alkyl halides extremely important as reagents in the preparation of other organic compounds. In this connexion, it should be noted that the iodides are the most reactive and the chlorides the least. Examples of the various reactions of the alkyl halides are shown below.

1. Reduction with nascent hydrogen (e.g. by means of a Zn/Cu couple and ethyl alcohol—see p. 863) gives the corresponding *paraffin*—

$$C_2H_5I + 2H = HI + \underset{\text{ethane}}{C_2H_6}$$

2. Removal of the halogen by sodium in ethereal solution (Wurtz Synthesis—*see* p. 863) produces, momentarily, the free alkyl radical, two of which unite to form the *higher paraffin*. Mixtures of alkyl halides similarly give mixtures of higher paraffins—

$$\left.\begin{matrix} C_2H_5{-}I \\ C_2H_5{-}I \end{matrix}\right\} + 2Na = C_4H_{10} + 2NaI$$

3. *Aqueous* potassium hydroxide slowly hydrolyzes the alkyl halide to

form the corresponding *alcohol*. This hydrolysis also occurs on boiling the halide with water.

$$C_2H_5I + KOH = C_2H_5OH + KI$$

4. *Alcoholic* potassium hydroxide, however, reacts differently to form the *olefine* (*see* p. 869)—

$$C_2H_5I + KOH = C_2H_4 + KI + H_2O$$

5. Sodium ethoxide reacts with alkyl halides to form *ethers*—

$$C_2H_5I + NaOC_2H_5 = NaI + \underset{\text{ether}}{C_2H_5OC_2H_5}$$

This is an example of Williamson's reaction.

6. Potassium cyanide reacts with alkyl halides to form compounds known as *nitriles or cyanides*—

$$C_2H_5I + KCN = KI + \underset{\substack{\text{ethyl cyanide}\\ \text{or propio-nitrile}}}{C_2H_5CN}$$

The name, propio-nitrile, is obtained from that of the fatty acid, i.e. propionic acid, which it produces by hydrolysis on boiling with dilute acids.

7. Silver cyanide on the other hand forms a class of compound known as *iso-nitriles or iso-cyanides*—

$$C_2H_5I + AgCN = AgI + \underset{\substack{\text{ethyl isocyanide}\\ \text{or}\\ \text{propio-isonitrile}}}{C_2H_5NC}$$

8. Silver nitrite reacts with alkyl halides to form a mixture of *nitrites* and *nitro-compounds*—

$$C_2H_5I + AgNO_2 \begin{cases} \nearrow \underset{\text{ethyl nitrite}}{C_2H_5 . O . NO} \\ \searrow \underset{\text{nitro-ethane}}{C_2H_5NO_2} \end{cases} + AgI$$

9. Ammonia reacts with the alkyl halides to form various *amines*—

$$C_2H_5I + HNH_2 = HI + \underset{\text{ethylamine}}{C_2H_5NH_2}$$

Of the other reactions that occur with alkyl halides mention only can be made here of the very important reactions which occur with (*a*) aceto-acetic ester, (*b*) Grignard reagents and (*c*) malonic ester.

The *di-halogen* derivatives of the paraffins, for example methylene chloride, CH_2Cl_2, are not important. They are prepared by the reduction of the corresponding, more easily prepared, tri-halogen derivative as, for example—

$$\underset{\text{chloroform}}{CHCl_3} + 2H = CH_2Cl_2 + HCl$$

Of the *tri-halogen derivatives* of the paraffins, chloroform and iodoform are particularly important.

Chloroform, $CHCl_3$, is prepared by the action of a hypochlorite, such as bleaching powder, on alcohol, acetaldehyde, ($CH_3 . CHO$) or acetone, (CH_3COCH_3). The hypochlorite behaves virtually as if it were composed of chlorine and the alkaline hydroxide, the following reactions taking place—

(*a*) *With alcohol.*

(i) Oxidation to acetaldehyde—

$$C_2H_5OH + Cl_2 = CH_3 . CHO + 2HCl$$

(ii) Chlorination of the methyl group of the acetaldehyde to give chloral—

$$CH_3 . CHO + 3Cl_2 = CCl_3 . CHO + 3HCl$$

(iii) Hydrolysis of the chloral by the alkali to give chloroform and the formate—

$$CCl_3CHO + NaOH = CHCl_3 + \underset{\text{sodium formate}}{H . COONa}$$

(*b*) *With acetaldehyde.* The reactions are those of (ii) and (iii) above.

(*c*) *With acetone.* Two stages may be traced here—

(i) Chlorination of one of the methyl groups—-

$$CH_3 . CO . CH_3 + 3Cl_2 = CCl_3 . CO . CH_3 + 3HCl$$

(ii) Hydrolysis with the alkali—

$$CCl_3CO . CH_3 + NaOH = CHCl_3 + \underset{\text{sodium acetate}}{CH_3 . COONa}$$

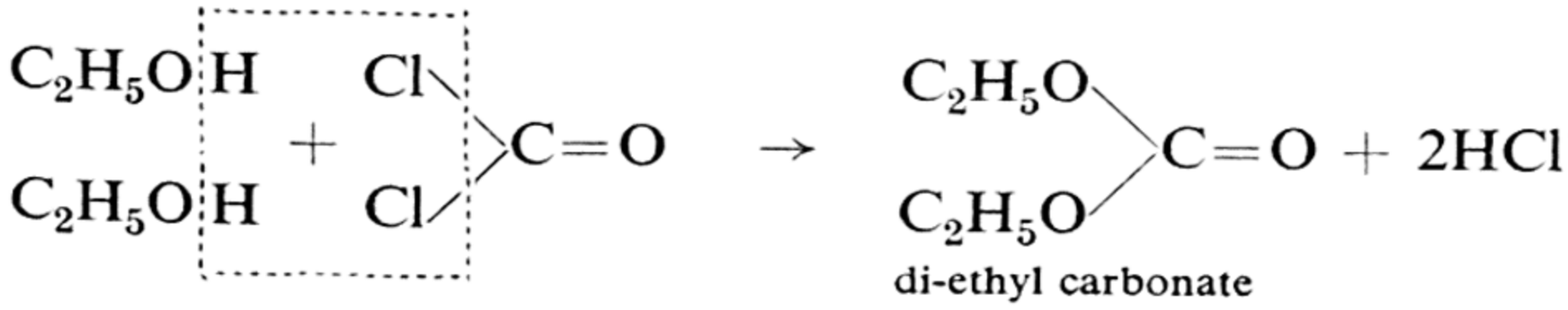
Since acetone is cheaper than acetaldehyde or alcohol, it is usual to prepare chloroform by this latter method using bleaching powder. The

bleaching powder is made up to a thin paste with water, and the acetone added. The flask is fitted with an upright reflux condenser. After a few minutes the reaction usually starts spontaneously and it may be necessary to moderate the reaction in the early stages by dipping the flask into cold water. When the initial fairly vigorous reaction has subsided, the flask is then heated on a boiling-water bath for a further 5–10 min to complete the reaction. The apparatus is then rearranged, as in Fig. 261, p. 885, and the chloroform distilled over. The chloroform, which usually contains some hydrochloric acid, is neutralized by shaking with a dilute solution of sodium hydroxide, and the heavy chloroform layer than separated and dried over anhydrous calcium chloride. Pure chloroform may then be obtained by redistillation, the fraction boiling between 60°–63°C being collected.

Properties of Chloroform. Chloroform is a colourless liquid, boiling point 61°C, and has a characteristic sweetish smell. It is used in organic chemistry as a solvent, and in medicine as an anaesthetic. The tendency of chloroform to decompose slowly on exposure to air and light to form the very poisonous carbonyl chloride (or phosgene, $COCl_2$)

$$CHCl_3 + O = COCl_2 + HCl$$

is counteracted by storing the chloroform in well-stoppered dark-blue or brown glass bottles. About 2 per cent of alcohol is also added to reduce the rate of this decomposition and to convert any phosgene into the relatively harmless diethyl carbonate—



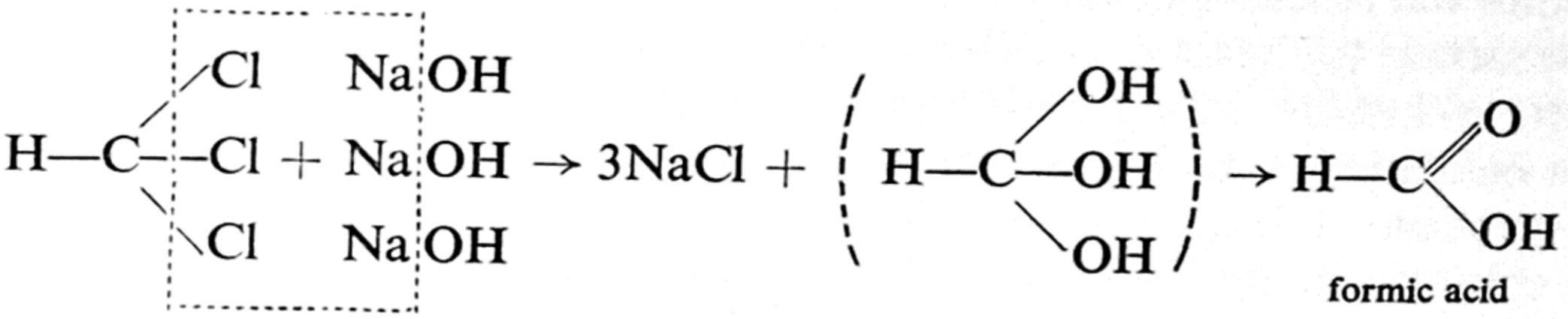
di-ethyl carbonate

Chemically, the most characteristic reaction of chloroform is the formation of an evil-smelling isocyanide when it is warmed with alcoholic sodium hydroxide and a primary amine, such as aniline, $C_6H_5NH_2$.

$$CHCl_3 + R\,.\,NH_2 + 3NaOH = R\,.\,NC + 3NaCl + 3H_2O$$

Since the isocyanide odour is extremely persistent and also poisonous this reaction should be carried out in a test-tube with only small quantities of the reagents (e.g. a few drops of aniline are quite sufficient). Once the odour of the isocyanide has been detected, the test-tube should be cooled and excess of concentrated hydrochloric acid carefully added to destroy the isocyanide. The isocyanide or, as it is also called, carbylamine reaction is specific for primary amines, but not for chloroform since iodoform, carbon tetrachloride, etc. behave similarly.

When chloroform is heated with aqueous alkalis, hydrolysis occurs to form the corresponding salt of formic acid—



formic acid

$$H\,.\,COOH + NaOH \rightarrow H_2O + H\,.\,COONa$$

sodium formate

Iodoform, CHI_3, is prepared by methods similar to those described above for chloroform, except that potassium iodide is added in addition to the hypochlorite. The two latter may be considered to form the hypo-iodite, which then reacts with the alcohol or acetone, etc.

$$C_2H_5OH \xrightarrow{O} CH_3\,.\,CHO \xrightarrow{I} CI_3\,.\,CHO \xrightarrow{NaOH} CHI_3 + H\,.\,COONa$$

$$CH_3\,.\,CO\,.\,CH_3 \xrightarrow{I} CI_3\,.\,CO\,.\,CH_3 \xrightarrow{NaOH} CHI_3 + CH_3\,.\,COONa$$

The reaction may conveniently be carried out in a test-tube by adding sodium hypochlorite solution to a mixture of acetone, potassium iodide solution and sodium hydroxide solution. (*Note*, the NaOCl must be added last.) Crystals of iodoform (m. p. 120°C) soon begin to separate as a heavy pale-yellow solid with a characteristic odour. This *iodoform reaction* is often used as a test for compounds containing the groups CH_3—CH(OH)—, as, for example, in ethyl alcohol, and CH_3—CO—C$\lessdot$ as, for example, in acetone.

Iodoform is much used in surgery as an antiseptic agent.

Carbon Tetrachloride, CCl_4, is a colourless, pleasant-smelling liquid which finds considerable use industrially as a solvent and, on account of its non-inflammability, as the liquid filling in Pyrene fire-extinguishers. Since, however, it reacts explosively with molten sodium (chloroform also), pyrene fire-extinguishers must not be used against sodium fires (see also sodium-fusion test, p. 1021). Precaution should also be taken against the poisonous carbonyl chloride which is formed if used in connexion with magnesium fires—

$$CCl_4 + H_2O = COCl_2 + 2HCl$$

Carbon tetrachloride is prepared commercially—

(*a*) By passing chlorine into carbon disulphide in the presence of iodine or aluminium chloride as catalyst.

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$$

sulphur mono-chloride

(*b*) By the action of sulphur monochloride on carbon disulphide in the presence of iron as a catalyst.

$$CS_2 + 2S_2Cl_2 = CCl_4 + 6S$$

Solvent Properties of Chlorinated Hydrocarbons

Chlorinated hydrocarbons, as a class, are excellent solvents for oils, greases, waxes, rubber and many resins, and this property coupled with their non-inflammability accounts for their wide use in many industrial operations, such as metal degreasing and as solvents for the cellulose esters, rubber, resins, etc. The most important members of the group, in addition to carbon tetrachloride are ethylene dichloride, trichlorethylene ("Westrosol"), tetrachlorethane ("Westron") and tetrachlorethylene.

Solvent	Formula	Boiling Point (°C)
Methylene dichloride .	CH_2Cl_2	42·0
Chloroform . .	$CHCl_3$	61·2
Carbon tetrachloride .	CCl_4	76·8
Dichlorethane . .	$CH_2Cl \cdot CH_2Cl$	83·7
Tetrachlorethane. .	$CHCl_2 \cdot CHCl_2$	145·0
Trichlorethylene . .	$CHCl = CCl_2$	86·7
Tetrachlorethylene .	$CCl_2 = CCl_2$	120·0

Tetrachlorethane is formed by the direct action of chlorine on acetylene—

$$C_2H_2 + 2Cl_2 = CHCl_2—CHCl_2$$

in the presence of antimony pentachloride.

Trichlorethylene, $CHCl:CCl_2$, may be prepared from tetrachlorethane by warming with milk of lime—

$$C_2H_2Cl_4 — HCl \rightarrow CHCl:CCl_2$$

Because of its extremely high solvent properties for oils, grease, tars, gums, rubber and many resins, and its relatively low toxicity compared with other chlorinated hydrocarbons, trichlorethylene is by far the most extensively used organic degreasing solvent. It is not inflammable and does not form explosive mixtures with air. Its low specific heat and latent heat of vaporization make it especially useful in hot solvent and vapour degreasing plant. In addition, its low surface tension enables trichlorethylene to penetrate readily into materials and crevices thus increasing its degreasing efficiency.

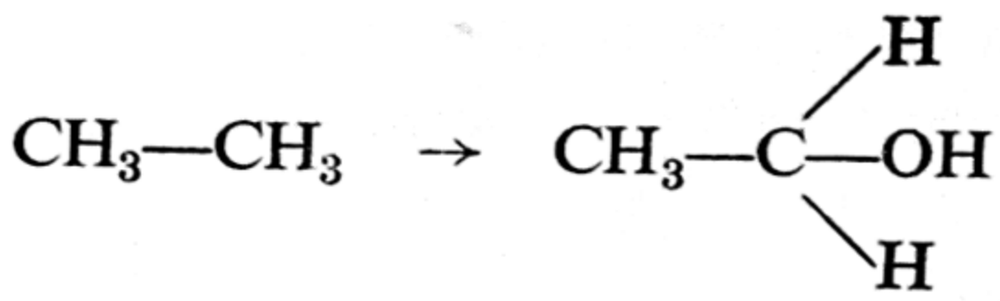
Pure trichloroethylene is used, as "Trilene," in gynaecological operations because of its mild anaesthetic properties.

CHAPTER 30

THE ALCOHOLS AND ETHERS

THE ALCOHOLS

The monohydric alcohols (or, simply, alcohols) may be regarded as paraffins in which one hydrogen atom has been replaced by the univalent hydroxyl group, (—OH). Thus, methane may be regarded as the parent of methyl alcohol, CH_3OH; ethane of ethyl alcohol, C_2H_5OH, and so on.



ethyl alcohol

Their general formula, therefore, is $C_nH_{2n+1}OH$. Ordinary alcohol is the second member of the series, and is more correctly known as ethyl alcohol.

Methyl Alcohol, CH_3OH, is known also as methanol and as wood spirit. It is obtained commercially by two processes—

1. *Destructive Distillation of Wood.* When wood is destructively distilled in iron retorts in the absence of air, the products obtained are—

(i) an inflammable gas, composed mainly of hydrogen and methane;
(ii) an aqueous distillate, known as pyroligneous acid;
(iii) wood-tar; and
(iv) a residue of wood-charcoal.

The approximate proportions of these four products are, respectively, 25, 45, 5 and 25 per cent.

Pyroligneous acid is a mixture of various compounds, the most important of which are methyl alcohol (1–2 per cent), acetic acid (10 per cent), acetone (0·1 to 0·5 per cent) and water. The acetic acid is first removed as the insoluble calcium acetate by adding milk of lime, and the liquid is then fractionally distilled to give crude methyl alcohol (or wood-spirit) containing about 70 per cent of methyl alcohol and 16 per cent of acetone together with small quantities of other organic compounds. Further careful fractional distillation serves to remove most of the acetone and other compounds, but if pure alcohol is required purification by chemical methods are necessary. One such method is to remove the methyl alcohol as its compound with calcium chloride, $CaCl_2 . 4CH_3OH$, which is separated by filtration. On subsequent heating, pure methyl alcohol is liberated and may be collected by condensing the vapours. It may then

be dried by means of quick-lime, and the last traces of water finally removed by treatment with metallic sodium.

2. *Synthetic Process.* Nowadays, most methyl alcohol is made by synthesis from carbon monoxide and hydrogen (for example, hydrogen-enriched water-gas). Water-gas, prepared by blowing steam through a bed of red-hot coke

$$\underset{\text{steam}}{C + H_2O} \rightarrow CO + H_2$$

is mixed with more hydrogen to bring the proportion of hydrogen to carbon monoxide in the gas up to the proportions required by the reaction—

$$CO + 2H_2 = CH_3OH$$

and then passed under very high pressures (of the order of 300 atmospheres, that is, 4500 lb/in.^{2}) through reaction vessels at 300°C containing a catalyst, such as copper mixed with oxides of zinc, aluminium, chromium or manganese. The issuing gases, containing more than 60 per cent of methyl alcohol, then pass under pressure to condensers which remove the methyl alcohol and permit the unchanged gases to be returned together with fresh gases, to the catalyst chambers. The alcohol produced by this process is very pure (99 per cent), but if the process is carried out at higher temperatures (greater than 350°C) increasing quantities of higher alcohols are produced at the same time.

Mention has been made earlier of the *Fischer-Tropsch* process (see p. 372) which also uses carbon monoxide and hydrogen as the starting materials. In this process, the mixture of carbon monoxide (1:2 by volume) is passed over a catalyst composed, for example, of cobalt (100 parts), thorium oxide (5 parts), magnesium oxide (8 parts) and kieselguhr (200 parts) at about 170 to 220°C *at ordinary pressures* to form a mixture of hydrocarbon vapours and steam. The ultimate products are similar to those obtained in the refining of petroleum, i.e. "gas oil," spirit, middle oil, heavy oil, soft wax, hard wax, etc.

Properties. Methyl alcohol is a colourless liquid, miscible with water in all proportions. It boils at 64·6°C, and burns in air with a pale non-luminous flame. It is neutral in its reactions. Unlike ethyl alcohol (or "alcohol"), methyl alcohol is poisonous and its consumption may lead to blindness, insanity and eventual death. It is used commercially as a denaturant for ethyl alcohol (thereby rendering the latter unfit to drink), as an anti-freeze in motor-car engines, as a solvent for ethyl cellulose, shellac (spirit varnish), soft-formaldehyde resins, castor oil, etc., as a refrigerant (m.p. − 97°C) and also chemically as a methylating agent in the manufacture of other organic compounds.

Chemically, it reacts with metallic sodium to form sodium methoxide (CH_3ONa), and may be converted into the methyl halide via phosphorus

penta-chloride (or via red phosphorus and bromine or iodine). With concentrated sulphuric acid in the warm it forms methyl hydrogen sulphate and a little dimethyl sulphate—

$$CH_3OH + H_2SO_4 \rightarrow CH_3 . HSO_4 + H_2O$$
$$2CH_3OH + H_2SO_4 \rightarrow (CH_3)_2SO_4 + 2H_2O$$

With organic acids reaction occurs in the presence of a dehydrating agent to form the corresponding methyl ester (*see* p. 940)—

$$CH_3 . CO\boxed{OH + H}OCH_3 \rightarrow \underset{\text{methyl acetate}}{CH_3 . COOCH_3}$$

Methyl alcohol is easily oxidized, for example by permangante or dichromate to form formaldehyde and then formic acid—

$$CH_3OH \xrightarrow{O} \underset{\text{formaldehyde}}{H . CHO} \xrightarrow{O} \underset{\text{formic acid}}{H . COOH}$$

This oxidation may be demonstrated very neatly in the laboratory by lowering a glowing platinum spiral into a beaker containing slightly warmed methyl alcohol, as shown in the diagram. The oxidation occurs catalytically on the surface of the platinum wire, and the heat liberated is sufficient to keep the latter red-hot. The acrid odour of formaldehyde soon becomes noticeable. Methyl alcohol vapour and air mixture may similarly be ignited by contact with very finely divided platinum (platinum black) even at ordinary temperatures.

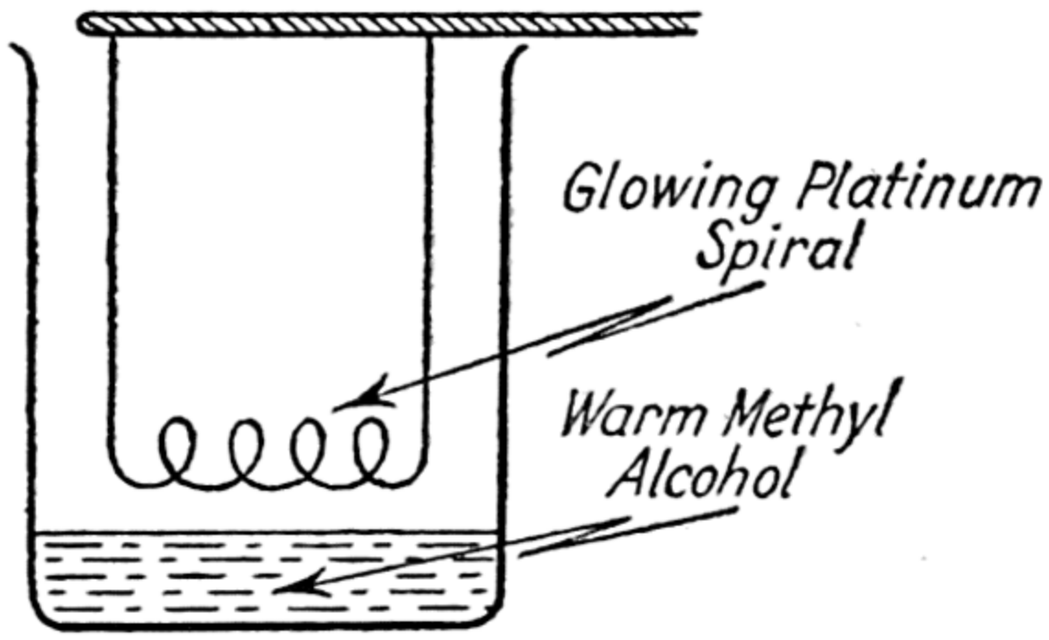


FIG. 262. Catalytic Oxidation of Methyl Alcohol

Formula of Methyl Alcohol

(*a*) Qualitative analysis (*see* p. 1021) shows methyl alcohol to be composed of carbon, hydrogen and oxygen.

(*b*) Quantitative analysis and determination of the vapour density shows the molecular formula to be CH_4O.

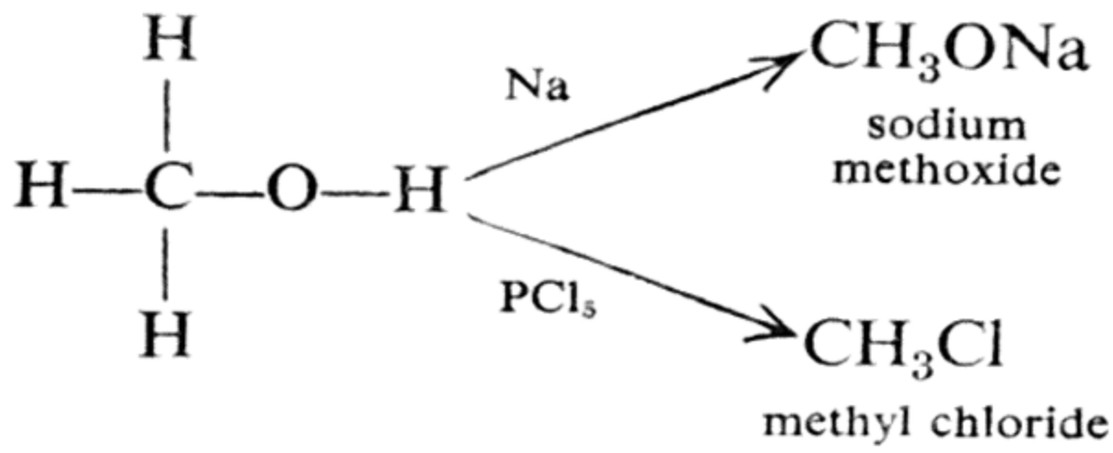
(*c*) Only one hydrogen atom is replaced by reaction with metallic sodium, so that this hydrogen atom must play a different role in the molecule than the three remaining hydrogen atoms—

$$2CH_4O + 2Na \rightarrow 2CH_3ONa + H_2$$

(*d*) Reaction with PCl_5 replaces one H and one O by a Cl atom—

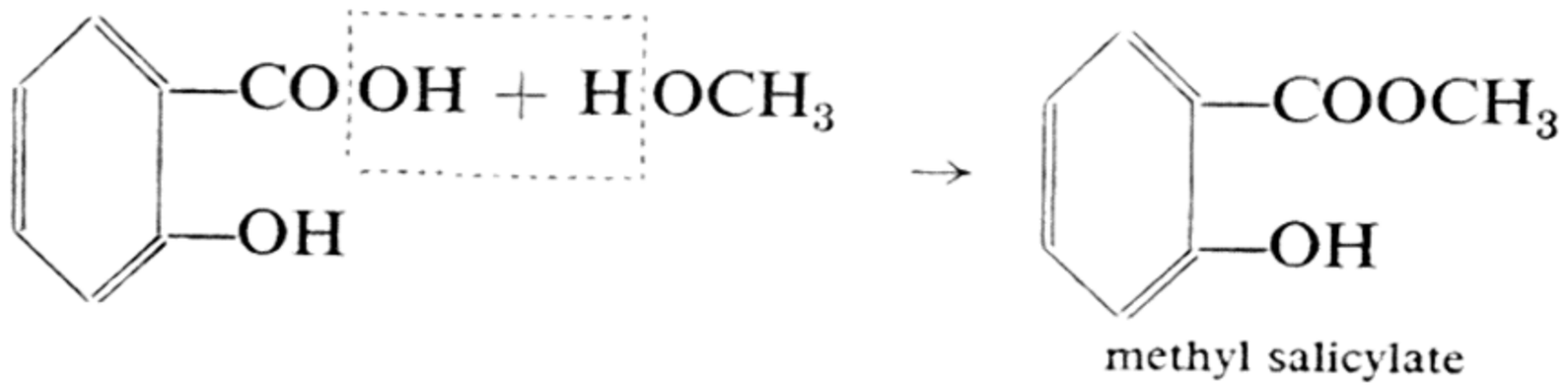
$$CH_4O (+ PCl_5) \rightarrow CH_3Cl$$

(*e*) These two reactions may be explained by giving methyl alcohol the formula—



Detection. Its reactions establish it to be an alcohol. It may be distinguished from the closely similar ethyl alcohol by—

(i) The formation of methyl salicylate ("Oil of Wintergreen," the familiar odour associated with most tooth-pastes) on warming with salicylic acid and a little concentrated sulphuric acid—



(ii) Methyl alcohol does not give the iodoform reaction (*see* p. 901); ethyl alcohol does.

Ethyl Alcohol, C_2H_5OH, the second member of the alcohol series, is by far the most important of these compounds and for this reason is often known simply as "alcohol." It is present in all alcoholic beverages (beers, wines, spirits, etc.) in concentrations varying from about 2 per cent to 40 per cent or more. Even larger quantities of the more or less pure alcohol are also produced nowadays for industrial usage. Although increasing quantities are being produced by direct synthesis (for example, from ethylene), the bulk of the world's supply of alcohol is still produced by the age-old method of fermenting certain sugars which are contained in, or may be obtained from, naturally occurring substances, such as starches, fruit juices, grain, sugar-beet, etc. The industry, however, has become very highly specialized in recent years, and fermentation is now a very important industrial method for producing not only alcohol but also such compounds as acetone, butyl alcohol, acetic acid, citric acid, lactic acid, and more recently penicillin.

Fermentation. The growth of our present-day knowledge of fermentation is mainly due to the fundamental work of Louis Pasteur, who showed that fermentation is directly caused by the life-processes of minute organisms, such as those present in yeast. These micro-organisms feed on organic materials and in the process convert these substances into different organic substances. The life of these organisms is very short (of the order of minutes) but this is compensated by their very high rate of reproduction.

In 1897 Büchner modified these views by showing that the living yeast cell is not necessary for fermentation, but that the clear liquid extracted from yeast under heavy pressure is equally capable of producing fermentation. This liquid extract owes its reactivity to the presence of certain very complex organic substances, which were termed *enzymes*. The growth of the living yeast cells result, therefore, in the production of these active enzymes, which in their turn bring about the very complex changes which occur during fermentation. These enzymes have been likened to organic catalysts, and just as there are numerous different catalysts for different reactions, so also are there numerous different enzymes, each with its own specific type of reactivity. The science of mycology is concerned with classifying these different enzymes and with studying the precise conditions under which bacteria, moulds, yeast, etc. may be made to produce particular selected strains best suited for each particular fermentation process. Once a desired strain has been isolated it must be preserved under carefully controlled conditions so that it reproduces only itself and not other less suitable strains. The colony so developed is then maintained as a sort of reservoir to satisfy the day to day demands of the industrial fermentation process for which it was developed. No longer will just any yeast do to make industrial alcohol or alcoholic drinks (beer, etc.); instead, carefully selected strains, grown under scientifically controlled conditions, are used so as to obtain the maximum efficiency of fermentation and the minimum of unwanted by-products.

Production of Alcohol by Fermentation. Alcohol is produced industrially by the alcoholic fermentation of various sugars, such as glucose, by the enzyme *zymase* present in living yeast cells. The reaction which occurs is—

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 + 31\,000 \text{ cal.}$$

but other reactions may occur to a limited extent depending on the strain of yeast used. Some acetic acid (vinegar) and glycerol are also formed in increasing quantities towards the end of the fermentation process, presumably by the fermentation reaction—

$$2C_6H_{12}O_6 + H_2O \rightarrow C_2H_5OH + CH_3 \,.\, COOH + 2C_3H_5(OH)_3 + 2CO_2$$

In the industrial production of alcohol other less expensive materials than glucose form the starting materials, the choice being determined in different parts of the world by the relative availability of these different materials. These latter fall, from their chemical nature, into two main classes—

(*a*) Substances rich in *starch*, such as potatoes (used mainly in Russia and in Germany), grain (such as barley and corn), rice, etc.

(*b*) Substances containing *sugars*, such as fruit juices, cane and beet sugar, or the molasses obtained from the manufacture of the latter (used principally in U.S.A. and in Britain).

Substances belonging to the starch family are first converted into sugars similar to those of the second group, and these then converted into alcohol by fermentation processes.

Considering potatoes as typical of the former class, these are made into a pulp and treated with superheated steam to break down the cellular plant structure and release the starch granules. The starch is then converted into fermentable sugars by one of the two methods (*a*) or (*b*) given below.

(*a*) By adding about 5 per cent of malt to the mash at about 50°–60°C. The enzyme *diastase* present in the malt converts the starch into malt-sugar or maltose, $C_{12}H_{22}O_{11}$, the process being complete in about a half an hour—

$$(C_6H_{10}O_5)_n \xrightarrow[\text{diastase}]{H_2O} C_{12}H_{22}O_{11}$$

(Malt is obtained by keeping moist barley in the dark at about 15°C until the induced germination has proceeded to the requisite stage, followed by a slow process of drying and "curing" in which the barley is heated over a period of days at increasing temperatures up to 90° to 110°C.)

(*b*) By boiling with dilute sulphuric acid, and subsequently neutralizing the acid, the product in this case being a mixture of two sugars, dextrose and maltose.

Yeast is then added to the sugar produced by either of the above methods and the fermentation allowed to proceed at a temperature not greater than 33°C for periods of the order of two to three days. During this period, the disaccharides (that is, sugars with the molecular formula, $C_{12}H_{22}O_{11}$) are first hydrolyzed to monosaccharides (that is, sugars with the formula $C_6H_{12}O_6$), and these latter then produce alcohol by alcoholic fermentation. The hydrolysis to the monosaccharides and the subsequent fermentation are brought about by particular enzymes present in the yeast. Thus, maltose is hydrolyzed by the enzyme *maltase*, cane-sugar or sucrose (present, for example, in the very important molasses or mother liquor of sugar manufacture) by the enzyme *invertase*, whilst the enzyme *zymase* effects the final conversion of the monosaccharides into alcohol and carbon dioxide—

(i) hydrolysis—

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$$

(ii) fermentation—

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

The alcoholic liquor produced at this stage is known as a "beer" and may contain from 6·5–8·5 per cent of alcohol. This alcohol is recovered by distillation processes to produce raw spirit containing about 90 per cent

alcohol. Further fractional distillation then yields "rectified spirit," which contains 95–95·6 per cent alcohol. No further increase in concentration beyond 95·6 per cent can be effected by fractional distillation of alcohol-water mixtures since at this composition the alcohol-water mixture distils unchanged. Alcohol containing 4·4 per cent of water is said to be a *constant boiling mixture*.

To produce absolute (i.e. anhydrous) alcohol, the modern process is to add some of a third liquid, such as benzene, and redistil. The water and benzene pass over first, leaving anhydrous alcohol behind in the distillation vessel. This process of *azeotropic distillation* has now almost entirely replaced the older process in which the 95 per cent alcohol was treated with quick-lime under pressure to remove the water, followed by distillation from fresh quick-lime.

Alcoholic Beverages. The manufacture of alcoholic beverages by fermentation processes follows a similar series of reactions to those described above. It should be noted, however, that a fermented liquor cannot contain more than 16–17 per cent of alcohol, since at this concentration the yeast is killed and the fermentation ceases. Beverages containing higher concentrations of alcohol are produced, therefore, either by fortifying the liquor by adding rectified spirit, or by distilling the liquor to produce spirits (such as whisky, brandy, etc.).

The earliest fermented liquors known in Britain were *mead* (from honey), *beer* (from barley) and *cider* (from apples), but *wines* produced by the fermentation of grapes were known in other parts of the world from the earliest times. The latter are produced by allowing the juice of grapes to ferment spontaneously on storage, the necessary enzymes being produced by organisms present on the grape-skins. *Brandy* is made by the distillation of wine made from a particular variety of grape, and may contain about 50 per cent of alcohol. *Whisky* is made similarly by distilling the fermented liquor obtained from malted barley and yeast. *Rum* is made by fermenting treacle or molasses and twice distilling the product; its peculiar "rum" flavour is due to traces of formic and butyric esters. *Vodka* is made by distilling the fermented liquor from potatoes, whilst *gin* is made by adding juniper berries and other substances such as liquorice to alcohol and redistilling, the alcoholic distillate then containing various flavouring matters extracted from these substances. *Liqueurs* are made by dissolving large quantities of sugar in alcohol and subsequently adding various flavouring and colouring materials.

Production of Alcohol from Ethylene. A newer process, likely to increase in importance, prepares alcohol from ethylene which is obtained by the catalytic cracking of petroleum and also from coke-oven gases, by the reaction—

$$C_2H_4 + \underset{\text{steam}}{H_2O} \rightarrow C_2H_5OH$$

This reaction is carried out by passing a mixture of ethylene and steam (1:2 by volume) under high pressure through a suitable reaction vessel at a temperature of about 200°C. About 20 per cent conversion of the gases to alcohol occurs. The uncombined gases, however, are not wasted but are returned together with fresh gas mixture to the reaction vessel.

This process, however, suffers from the disadvantage of requiring a relatively concentrated source of ethylene. Weaker sources, containing as low as 30 per cent of the gas, are best treated by the indirect process. The ethylene is absorbed in 90 per cent sulphuric acid to form ethyl hydrogen sulphate and some diethyl sulphate—

$$3C_2H_4 + 2H_2SO_4 \rightarrow C_2H_5HSO_4 + (C_2H_5)_2SO_4$$

The liquid product is then hydrolyzed by diluting and heating, and the resulting alcohol (and ether) then separated by distillation. The process suffers from the disadvantage of handling, and having to concentrate, large quantities of sulphuric acid.

Properties of Ethyl Alcohol. Ethyl alcohol is a colourless liquid, b.p. 78°C, and burns in air with a hot, pale-blue flame. Like methyl alcohol it is miscible with water in all proportions, but in the case of the higher alcohols, the solubility decreases with increase in molecular weight. Alcohol is the intoxicating principle in all alcoholic beverages and in an effort to control the indiscriminate consumption of these liquors a heavy tax or duty is imposed in most countries. Considerable quantities of tax-free alcohol are used, however, solely for undustrial purposes.

To prevent illegal use of this alcohol as a beverage, it is denatured by the addition of various substances which make it dangerous to drink. The principal denaturant is methyl alcohol, but small quantities of other substances, such as pyridine and various dyestuffs, are also added to impart a disagreeable odour and taste. Methylated spirit (or industrial alcohol), for example, consists of ethyl alcohol to which has been added about 5 per cent of wood spirit (mainly methyl alcohol). Mineralized methylated spirit contains about 10 per cent of wood spirit together with small quantities of pyridine, paraffin oils and dyestuffs. It should be noted that all forms of denatured alcohol are very poisonous.

Chemically, the principal reactions of ethyl alcohol are those already described for methyl alcohol, i.e.—

1. Reaction with metallic sodium (or potassium)—

$$2C_2H_5OH + 2Na = H_2 + \underset{\text{sodium ethoxide}}{2C_2H_5ONa}$$

2. Reaction with phosphorus halides—

$$C_2H_5OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl$$

$$C_2H_5OH\ (+ P + I_2) \rightarrow C_2H_5I$$

3. Reaction with acids to form *esters*—

$$\text{alcohol} + \text{acid} \rightleftharpoons \text{ester} + \text{water}$$

$$C_2H_5OH + HCl \rightarrow C_2H_5Cl + H_2O$$

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$

$$C_2H_5OH + CH_3 . COOH \rightarrow CH_3 . COOC_2H_5 + H_2O$$

These reactions in which an alcohol reacts with an acid are known as *esterification* reactions. They are reversible and, under appropriate conditions, the resulting ester may be hydrolyzed back to the alcohol and acid.

The student should compare the following two reactions—

$$\text{Base} + \text{Acid} \rightarrow \text{Salt} + \text{Water}$$

$$NaOH + HCl \rightarrow NaCl + H_2O$$

$$\text{Alcohol} + \text{Acid} \rightarrow \text{Ester} + \text{Water}$$

$$C_2H_5OH + HCl \rightarrow C_2H_5Cl + H_2O$$

The formal similarity of these two equations suggests that the ester is the organic counterpart of the inorganic salt. This analogy, however, should not be pushed any further since an alcohol is not a base, the ester is not a salt (it is, in fact, a purely covalent compound, insoluble in water and soluble in organic solvents), and, finally, the reaction itself occurs only slowly and is certainly not ionic.

4. Oxidation converts ethyl alcohol into acetaldehyde, further oxidation of the latter then producing acetic acid—

$$C_2H_5OH \xrightarrow{O} \underset{\text{acetaldehyde}}{CH_3 . CHO} \xrightarrow{O} \underset{\text{acetic acid}}{CH_3 . COOH}$$

This reaction may be carried out, for example, by warming a mixture of potassium dichromate, dilute sulphuric acid and one to two millilitres of ethyl alcohol in a test-tube.

The above reactions are general for all alcohols. Additional important reactions of ethyl alcohol include the following—

With concentrated sulphuric acid, ethyl alcohol may be converted, by the intermediate formation of ethyl hydrogen sulphate, either into ethylene (*see* p. 869), or into di-ethyl ether (*see* p. 904), depending upon the conditions, namely—

100°C: formation of ester—

$$C_2H_5OH + H_2SO_4 = C_2H_5 . HSO_4 + H_2O$$

140°C and excess alcohol: formation of ether—

$$C_2H_5 . HSO_4 + HOC_2H_5 \rightarrow O\begin{matrix}C_2H_5\\C_2H_5\end{matrix} + H_2SO_4$$

160°C and excess sulphuric acid: formation of ethylene—

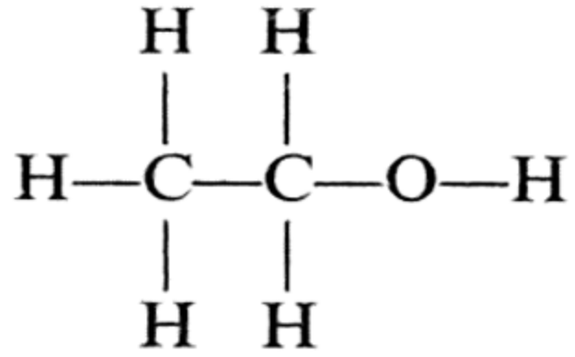
$$C_2H_5 . HSO_4 \rightarrow C_2H_4 + H_2SO_4$$

Iodoform reaction (*see* p. 890).

$$C_2H_5OH \xrightarrow{O} CH_3 . CHO \xrightarrow{I_2} CI_3 . CHO \xrightarrow{NaOH} CHI_3 + H . COONa$$

The reaction may be carried out in a test-tube by mixing ethyl alcohol, aqueous potassium iodide and sodium hydroxide solution, followed by sodium hypochlorite solution and gently warming. Pale yellow crystals of iodoform soon separate.

Formula of Ethyl Alcohol. That ethyl alcohol has the formula—

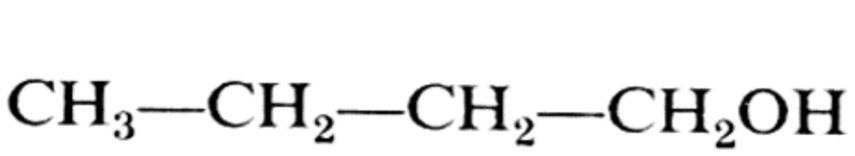


may be shown by arguments similar to those put forward for methyl alcohol.

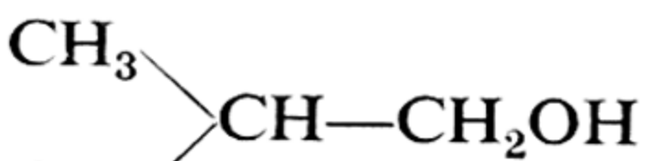
Uses of Ethyl Alcohol. These may be classified into the four main categories of solvent, chemical intermediate, fuel and alcoholic beverages. Ethyl alcohol is extremely important as an industrial solvent. It is used to dissolve resins and shellac in the manufacture of lacquers, varnishes, etc., and as a solvent in the manufacture of hair-washes, transparent soaps, perfumes, and other cosmetic preparations. It is used as the parent compound in the manufacture of such compounds as acetone, acetic acid, ether, chloroform and butyl alcohol, etc., and as an intermediate in the manufacture of various dyestuffs and pharmaceutical products. Its usage as a fuel, for example in internal combustion engines, is limited mainly by the danger of its being diverted to illegal usages, but in many countries without natural petrol resources quantities (from 10–20 per cent) are added to conserve the petrol supplies. Petrol containing greater proportions of alcohol are used as the fuel in all modern high-speed engines, for example in speed-way cars and motor-cycles.

Isomerism in the Alcohol Series

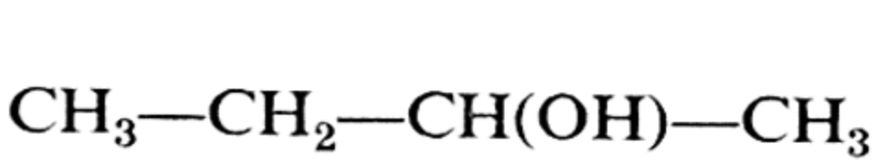
Isomerism occurs with the higher alcohols due to (*a*) carbon-chain isomerism, and (*b*) position of the (OH) radical in the carbon chain. Thus butyl alcohol has four isomers—



n-butyl alcohol



iso-butyl alcohol

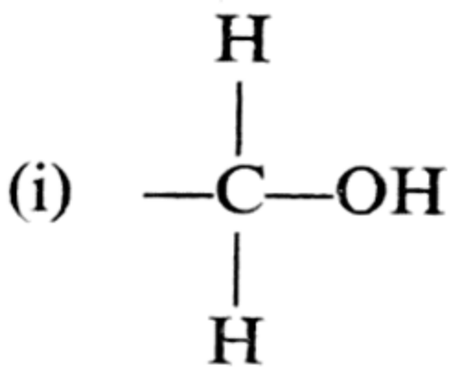
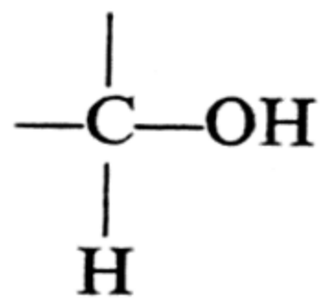
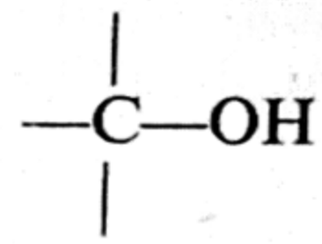


secondary butyl alcohol

tertiary butyl alcohol

Amyl alcohol similarly has eight isomers, the number of isomers increasing rapidly with ascent of the series.

Nomenclature. Considering the carbon atoms to which the (OH) radicals are attached in the above examples, it will be seen that these may be classified into three types—

(i)  (ii)  and (iii) 

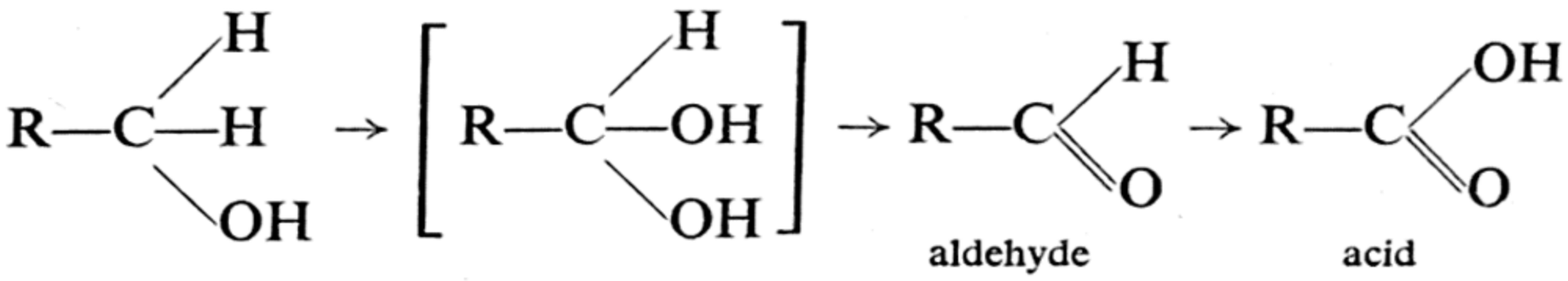
Alcohols of the first type are known as *primary* alcohols; they are characterized by having the group, $—CH_2OH$, in which the carbon atom is singly linked to one other carbon atom.

Alcohols of the second type are known as *secondary* alcohols; they are characterized by having the group $>CHOH$, in which the carbon atom is singly linked to two other carbon atoms.

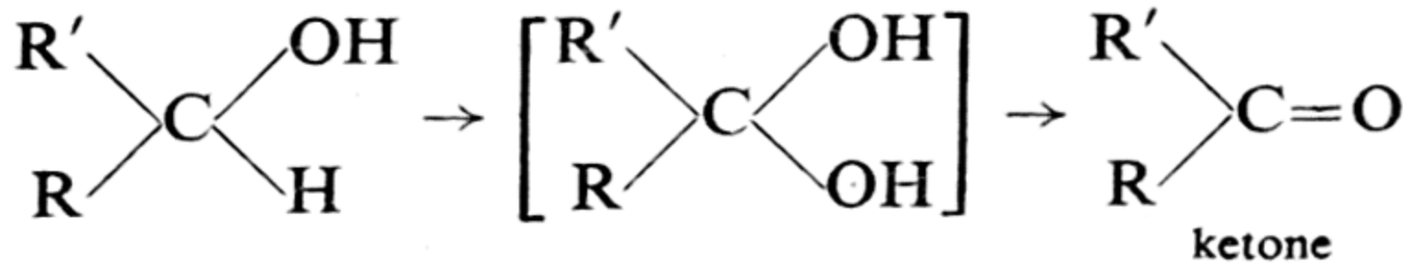
Alcohols of the third type are known as *tertiary* alcohols; they are characterized by having the group, $\geqslant C—OH$, in which the carbon atom is attached to three other carbon atoms.

Distinction between Primary, Secondary and Tertiary Alcohols

Behaviour on Oxidation. Primary alcohols are easily oxidized to aldehydes and fatty acids which contain the same number of carbon atoms—



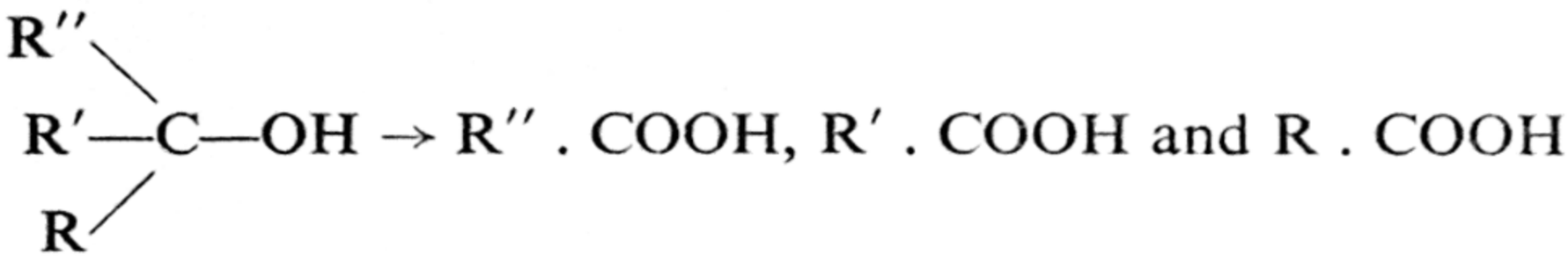
Secondary alcohols are easily oxidized to ketones. Further oxidation only occurs with powerful oxidizing agents and results in fatty acids containing fewer carbon atoms—



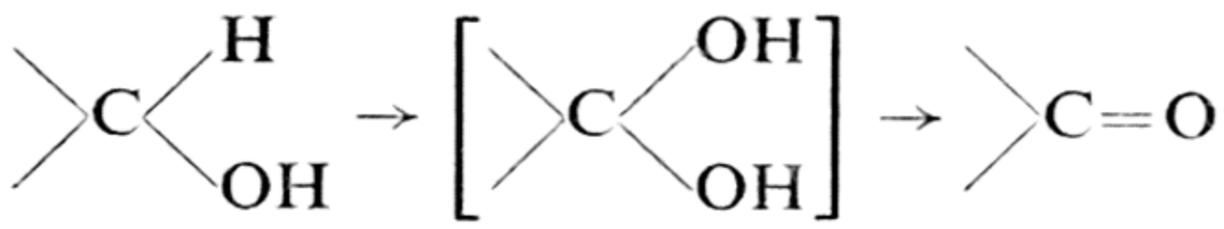
and with powerful oxidizing agents

Tertiary alcohols are *not* easily oxidized. Very strong oxidizing agents

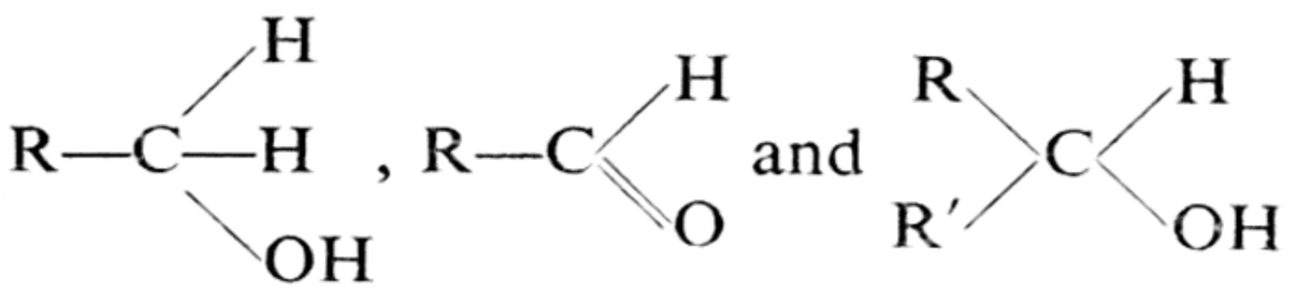
disrupt the molecule to give a mixture of fatty acids each of lower carbon content than the initial alcohol—



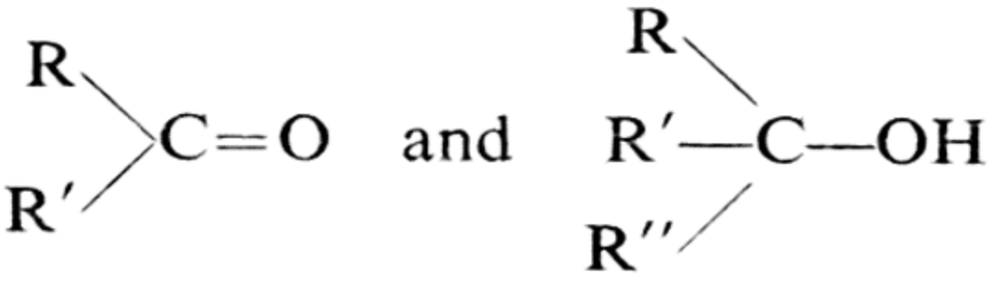
Note. The alcohols are easily oxidized if the C atom containing the hydroxyl radical also contains a hydrogen atom. This latter is oxidized to hydroxyl. If the resulting compound now contains two hydroxyl groups attached to the same carbon atom, it is unstable and loses a molecule of water to form a carbonyl (>C=O) group, e.g.—



Compounds, such as



are thus easily oxidized, whereas compounds, such as



are not.

Nitro-paraffin Test. The alcohol is converted into the alkyl iodide and thence, by distilling with silver nitrite, into the corresponding nitro-compound—

Primary alcohol

$$—CH_2OH \rightarrow —CH_2I \rightarrow —CH_2 . NO_2 \quad . \quad . \quad (a)$$

Secondary alcohols

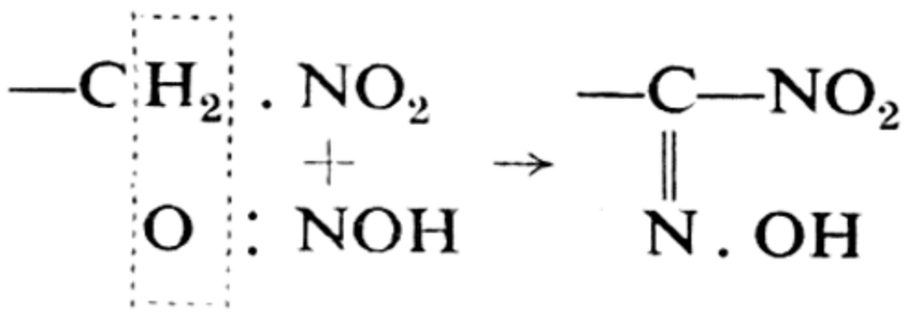
$$>CHOH \rightarrow >CHI \rightarrow >CH . NO_2 \quad . \quad . \quad (b)$$

Tertiary alcohols

$$\geqslant COH \rightarrow \geqslant C . I \rightarrow \geqslant C . NO_2 \quad . \quad . \quad . \quad (c)$$

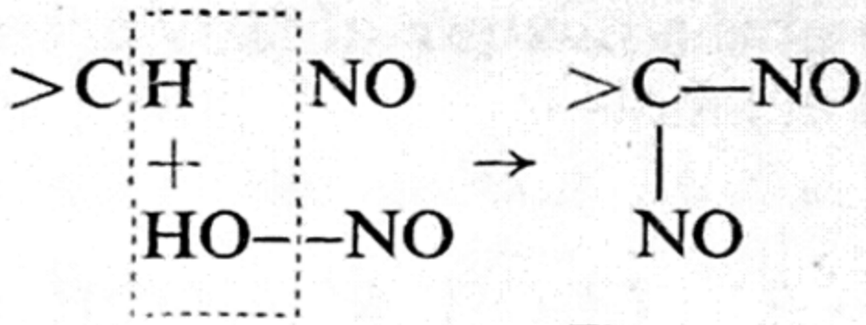
These nitro-compounds are then treated with nitrous acid, with which they react as follows—

(*a*)



These compounds, known as *Nitrolic acids*, dissolve in alkalis to form dark red solutions.

(*b*)

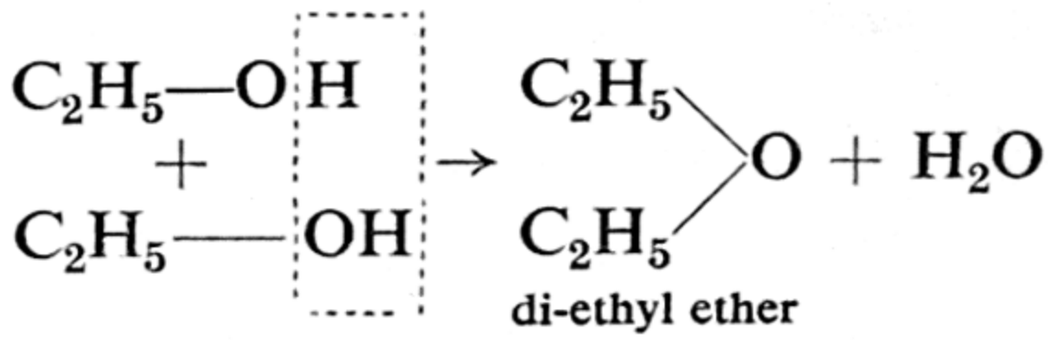


These compounds, known as *pseudo-nitrols*, dissolve in alcohol, ether, etc., to give blue solutions.

(*c*) $\geqslant C \,.\, NO_2$ does not react with nitrous acid.

THE ETHERS

The *ethers* are compounds of the type $CH_3—O—CH_3$, in which two alkyl groups are linked together through an oxygen atom. When the two alkyl groups are the same, the ether is said to be simple, but when the alkyl groups are different the ether is said to be a mixed ether. The ethers may be regarded as partial dehydration products of the alcohols, thus—



Di-ethyl ether is by far the most important of the ethers and is often referred to simply as "ether."

Preparation of Di-ethyl Ether

1. *From Alcohol.* Ethyl alcohol is slowly added to a mixture of concentrated sulphuric acid and ethyl alcohol heated to 140°C in apparatus as shown in the diagram opposite.

$$C_2H_5OH + H_2SO_4 = C_2H_5 \,.\, HSO_4 + H_2O$$

$$C_2H_5 \,.\, HSO_4 + HOC_2H_5 = C_2H_5 \,.\, O \,.\, C_2H_5 + H_2SO_4$$

Since, theoretically, the sulphuric acid is not used up in this reaction, it is often referred to as the *continuous etherification process.* In practice, however, various side reactions occur with reduction of some of the sulphuric acid, and in addition the sulphuric acid becomes progressively weaker, so that if large quantities of ether are being produced additional

small quantities of concentrated sulphuric acid would have to be added periodically.

The mixture of ether, water, unchanged alcohol and some sulphur dioxide which distils over is condensed and collected. After shaking with a solution of sodium hydroxide to remove the sulphur dioxide and some of the alcohol, the upper ether layer is then separated and dried over anhydrous calcium chloride (which also removes any residual alcohol). The dry ether is then redistilled and the fraction boiling between 34° to 39°C collected.

Note: Special precautions against explosions and fire must always be observed when preparing and using ether. The liquid is very volatile and

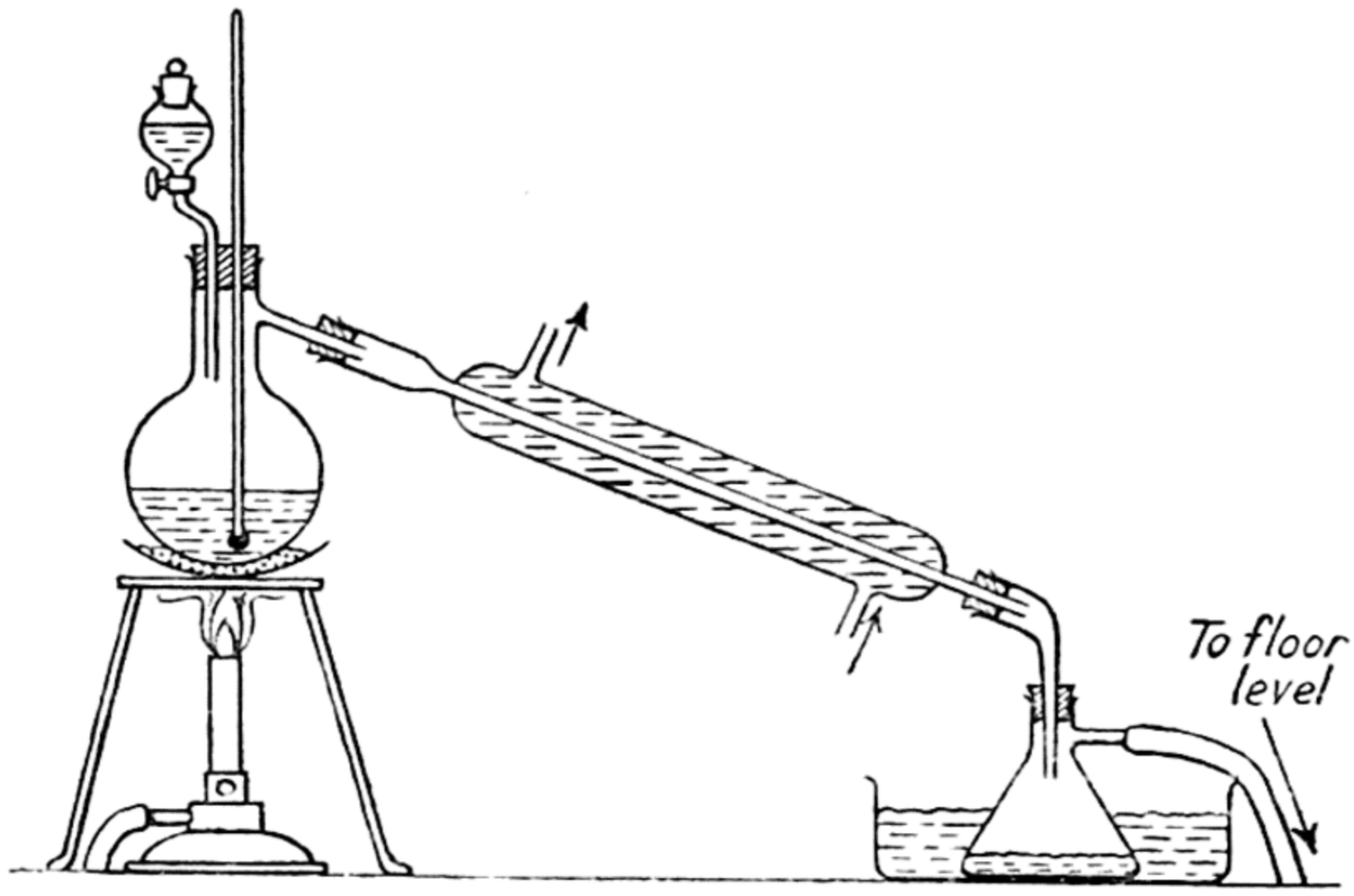


FIG. 263. Preparation of Ether

inflammable, and its vapour forms highly explosive mixtures with the air. This mixture may explode even when it has drifted some distance from its origin. In the above preparation, therefore, it is a necessary precaution to attach a length of rubber tubing to the receiving flask so as to conduct any uncondensed ether vapours to floor level away from contact with flame.

2. *From Alkyl Iodides*

(*a*) By Williamson's synthesis. This involves heating a mixture of the alkyl iodide and sodium alcoholate in alcoholic solution. The ether which distils over is collected and treated as above.

$$R—O\boxed{Na + I}—R' \rightarrow R—O—R' + NaI$$

$$C_2H_5—O\boxed{Na + I}—C_2H_5 \rightarrow C_2H_5—O—C_2H_5 + NaI$$

(*b*) By gently heating the alkyl halide with dry silver oxide.

$$\begin{matrix} C_2H_5I \\ C_2H_5I \end{matrix} + \begin{matrix} Ag \\ Ag \end{matrix}\!\!>\!O \rightarrow \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O + 2AgI$$

Properties. Di-ethyl ether (or "ether") is a colourless mobile liquid which boils at + 35°C. It has a characteristic pleasant smell but the vapour if inhaled produces unconsciousness and this explains its use as an anaesthetic (in conjunction with chloroform and alcohol, or with nitrous oxide and oxygen). Very low temperatures may quickly and easily be produced by rapidly evaporating liquid ether, for example, by blowing air through ether. Ether is only slightly soluble in water (alcohol is miscible in all proportions), and this limited solubility, coupled with its excellent solvent properties for organic substances, makes ether particularly valuable for extracting such substances from aqueous solutions or suspensions. Thus, on shaking these solutions with ether, the organic substances dissolve preferentially in the ether. The upper layer of ether is separated via a separating funnel and the ether then removed by distillation or evaporation.

Ether is very inflammable and its vapour forms explosive mixtures with air. As described above, special precautions must, therefore, be adopted when handling ether to avoid explosions and fires.

Apart from this ease of ignition in air, ether is characterized by almost complete indifference to most of the common chemical reagents. Thus, it does not react with metallic sodium, with alkalis, nor with weak acids, whilst reaction with phosphorus pentachloride occurs only slowly on heating—

$$C_2H_5—O—C_2H_5 + PCl_5 \rightarrow 2C_2H_5Cl + POCl_3$$

Reaction also occurs slowly on saturating ether with hydrogen iodide gas—

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O + \begin{matrix} H\,I \\ H\,I \end{matrix} \rightarrow 2C_2H_5I + H_2O$$

Ether is not attacked by the ordinary oxidizing or reducing agents, but ozone converts it into an explosive peroxide.

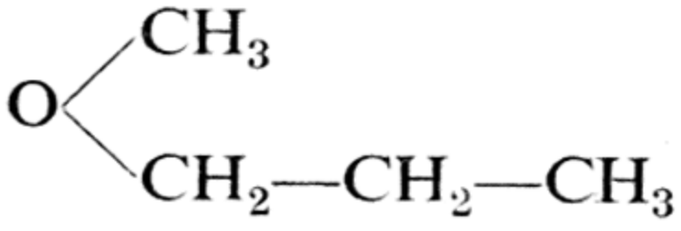
Formula of Di-ethyl Ether

(*a*) Williamson's synthesis from ethyl iodide and sodium ethoxide suggests the formula $CH_3—CH_2—O—CH_2—CH_3$ in which the two alkyl radicals are linked together through an oxygen atom.

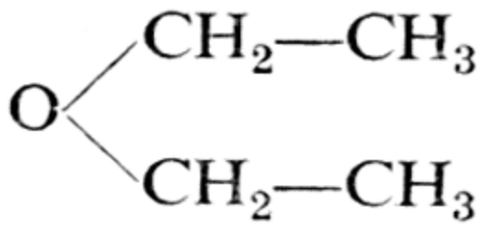
(*b*) The alternative formula in which the oxygen is present as a hydroxyl (—OH) group, is disproved by the non-reactivity of ether with metallic

sodium, and also by its difficult reaction with phosphorus pentachloride in which no HCl is liberated. (Compounds containing the OH group react with PCl_5 to form the corresponding chloride *with evolution of HCl*, and this reaction is often used to indicate the presence of this group in a molecule.)

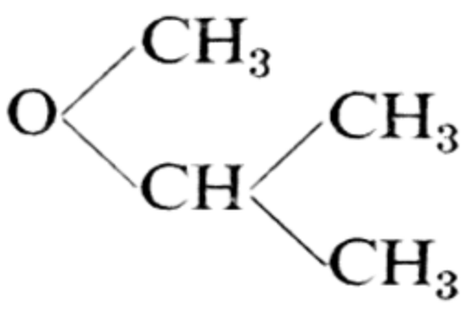
Isomerism. A new type of isomerism, known as *metamerism* occurs in the ethers. Metamerism is defined as isomerism involving radicals attached to a polyvalent element (e.g. —O—, —S—, etc.) in which the compounds are all of the same chemical type. Thus in the following examples, the compound having the formula $C_4H_{10}O$ may be any one of seven different compounds, which are therefore all isomers. The first three, however, are also ethers involving a di-valent oxygen atom and are known as metamers. The distinction is made clearer, perhaps, by the alternative definition of metamerism as isomerism in which all the carbon atoms are *not* directly united.



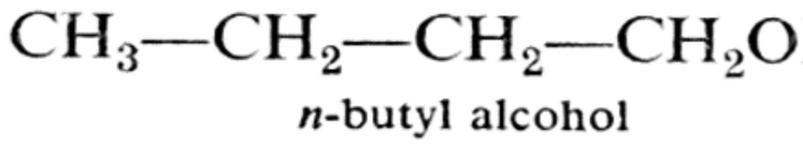
n-propyl methyl ether



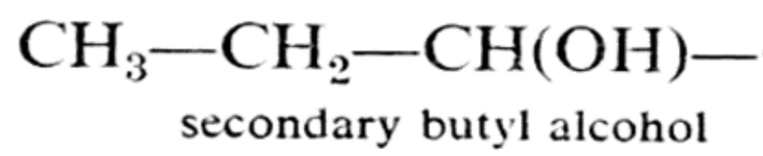
di-ethyl ether



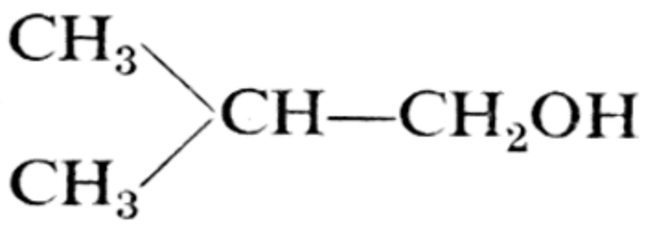
iso-propyl methyl ether



n-butyl alcohol



secondary butyl alcohol



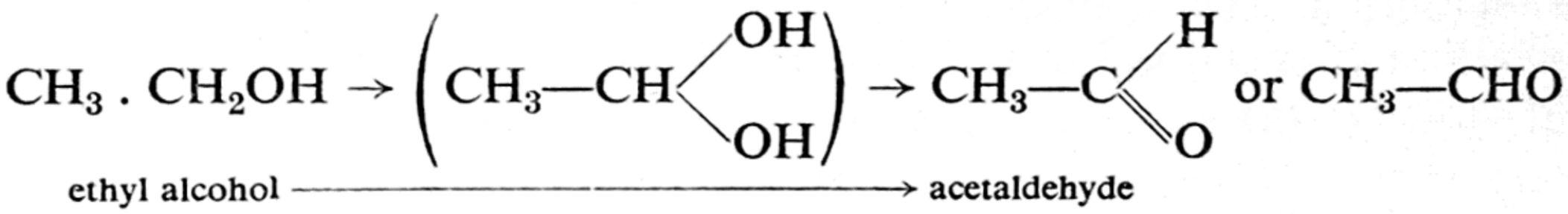
iso-butyl alcohol

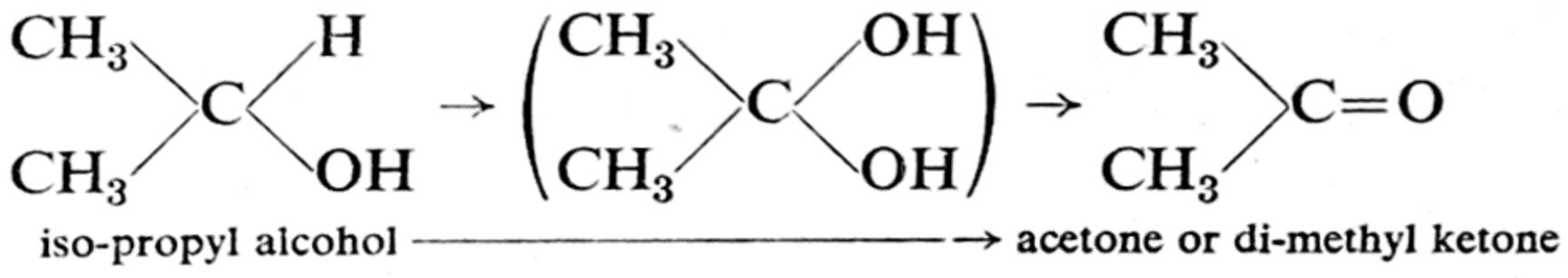
tertiary butyl alcohol

CHAPTER 31

ALDEHYDES AND KETONES

THE names *aldehydes* and *ketones* are given to two closely related classes of compound which have the same generic formula, $C_nH_{2n}O$. Both are formed by oxidation of the alcohols, the aldehydes from the primary alcohols and the ketones from the secondary alcohols.





It is seen from these two examples that both aldehydes and ketones have the oxygen atom present in a carbonyl (>C=O) group, and this fact accounts for many of the similarities in properties shown by these compounds. Many of the reactions of these two classes of compounds, however, are somewhat different, and these differences are due to the presence of an easily oxidized and reactive hydrogen atom on the carbonyl group in the aldehydes. Aldehydes are thus characterized by the presence of the univalent aldehyde group, —CHO, and ketones by the bivalent ketone or carbonyl group, >C=O as shown on p. 909.

General Methods for Preparing Aldehydes and Ketones

1. By oxidation of primary or secondary alcohols, for example, by potassium dichromate and sulphuric acid.

Primary alcohols

$$R—CH_2OH \rightarrow \text{Aldehydes } R—CHO$$

Secondary alcohols

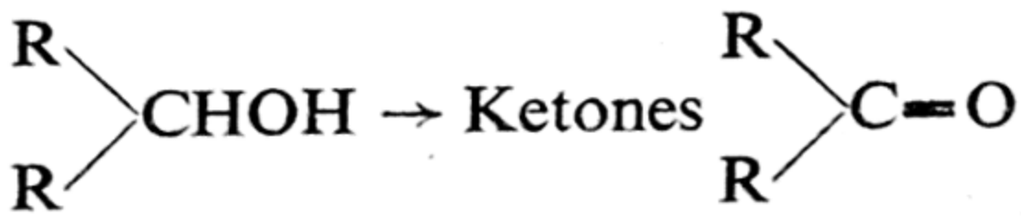


TABLE 116

Simple Aldehydes and Ketones

	Molecular Formula	Structural Formula	B.P. (°C)
Aldehydes			
Formaldehyde .	CH_2O	H—CHO	— 21·0
Acetaldehyde .	C_2H_4O	CH_3—CHO	+ 20·8
Propionaldehyde .	C_3H_6O	$CH_3 . CH_2$—CHO	+ 49·0
n-butyraldehyde .	C_4H_8O	$CH_3 . CH_2 . CH_2 . CHO$	+ 75·0
iso-butyraldehyde.	C_4H_8O	$(CH_3)_2 . CH$—CHO	+ 61·0
Ketones			
Acetone or di-methyl ketone .	C_3H_6O	$(CH_3)_2C = O$	+ 56·5
Methyl ethyl ketone . .	C_4H_8O	$\begin{matrix} CH_3 \\ \diagdown \\ \quad C = O \\ \diagup \\ C_2H_5 \end{matrix}$	+ 81·0
Di-ethyl ketone .	$C_5H_{10}O$	$\begin{matrix} C_2H_5 \\ \diagdown \\ \quad C = O \\ \diagup \\ C_2H_5 \end{matrix}$	+ 103·0

2. By distilling the calcium salt of the fatty acid *either alone* to give the ketone—

$$\begin{matrix} CH_3 . COO \\ \qquad\quad \diagdown \\ \qquad\quad\ Ca \\ \qquad\quad \diagup \\ CH_3 . CO\ O \end{matrix} \rightarrow \begin{matrix} CH_3 \\ \diagdown \\ \quad C{=}O \\ \diagup \\ CH_3 \end{matrix} + CaCO_3$$

or admixed with an equal quantity of calcium formate to give the aldehyde—

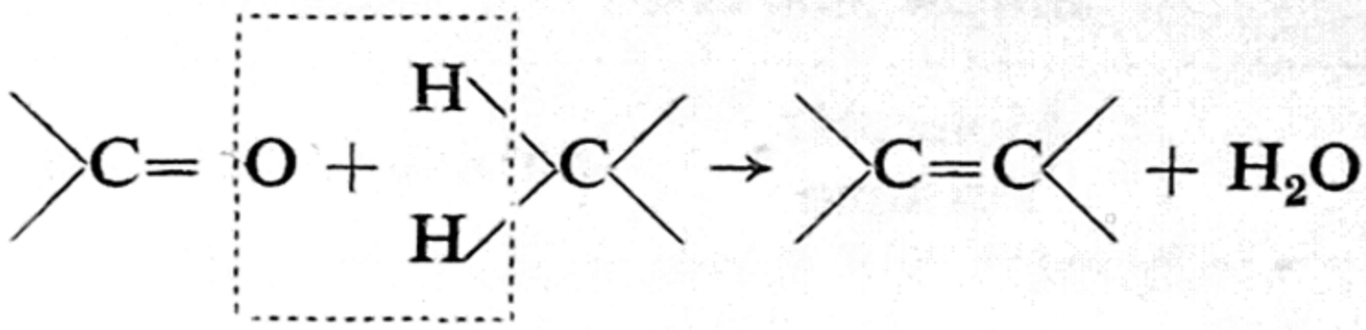
$$\begin{matrix} CH_3 . CO\ O \\ \qquad\quad \diagdown \\ \qquad\quad\ Ca \\ \qquad\quad \diagup \\ CH_3 . CO\ O \end{matrix} + \begin{matrix} OOC . H \\ \diagup \\ Ca \\ \diagdown \\ OOC . H \end{matrix} \rightarrow 2CH_3{-}CHO + 2CaCO_3$$

General Reactions shown by Both Aldehydes and Ketones

These are reactions which involve only the carbonyl group, and belong broadly to two types—

(*a*) $\quad \diagdown C{=}O \rightarrow \begin{matrix} | \\ -C- \\ | \end{matrix} OH$

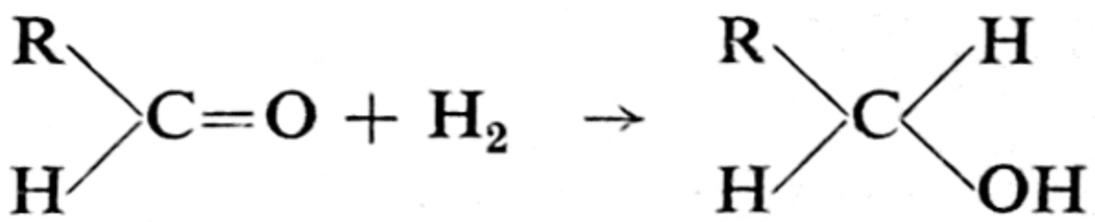
i.e. formation of an —OH group;

(*b*) 

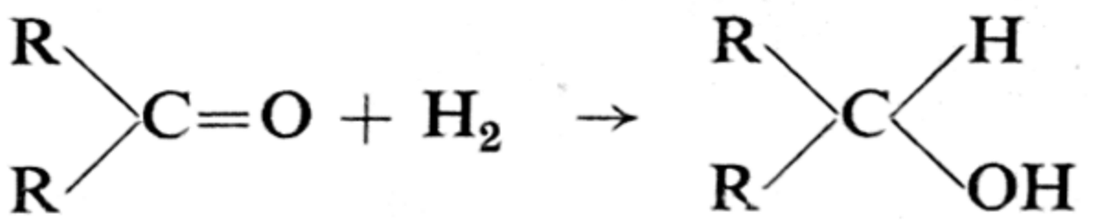
i.e. removal of the oxygen as water.

Reactions of type (*a*) *include*—

(i) *Reduction*, for example, by passing the vapour mixed with hydrogen over a finely divided nickel catalyst at about 200°C, converts the aldehyde and ketone to the alcohol—

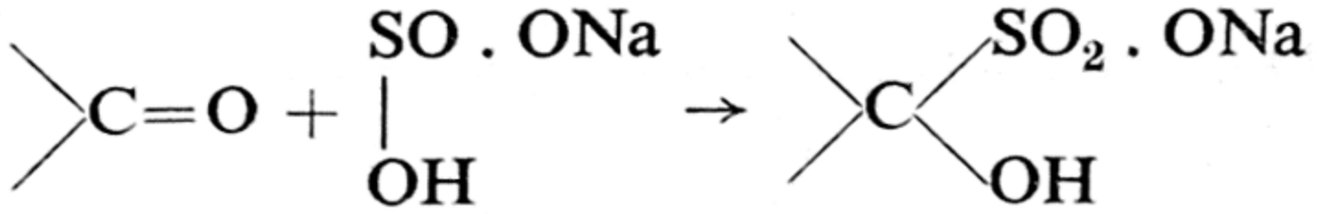


primary alcohol



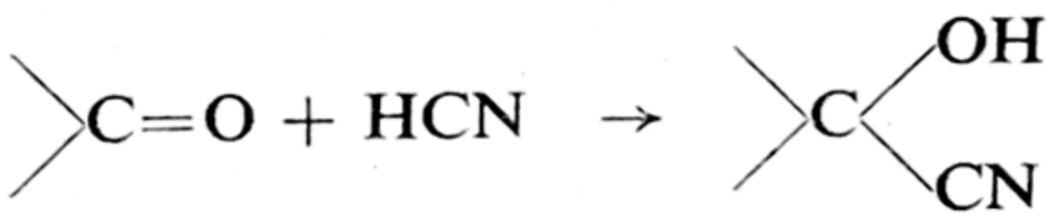
secondary alcohol

(ii) Formation of crystalline bisulphite compounds with sodium hydrogen sulphite solution—



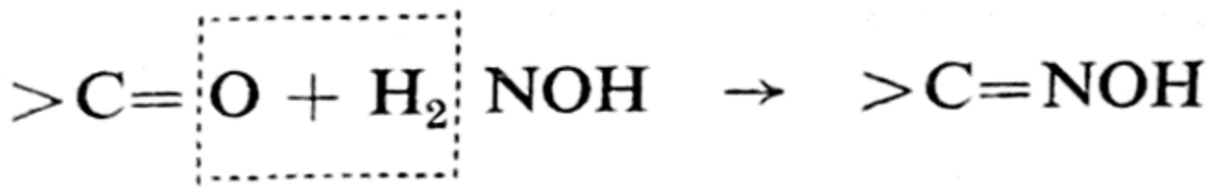
These bisulphite compounds crystallize easily (but not those of formaldehyde or acetaldehyde) and are useful in the separation and purification of aldehydes and ketones. When distilled with sodium carbonate, the aldehyde or ketone is liberated and may be collected.

(iii) Formation of *cyanhydrins* with hydrogen cyanide—



Reactions of type (*b*) *include*—

(i) Formation of *oximes* with hydroxylamine—



These are solid crystalline compounds with definite melting points, the determination of which often serves to identify the aldehyde or ketone.

(ii) Formation of *hydrazones* with hydrazine (or phenyl hydrazine)—

$$>C=O + H_2N . NH_2 \rightarrow >C=N . NH_2$$

$$>C=O + H_2N . NHC_6H_5 \rightarrow >C=N . NHC_6H_5$$

Aldehydes and ketones also react with phosphorus pentachloride to form aldo- and keto-chlorides respectively—

$$>C=O + PCl_5 \rightarrow >C\begin{matrix}Cl\\Cl\end{matrix} + POCl_3$$

Note, that HCl is not liberated in this reaction, and this fact indicates the absence of the hydroxyl (— OH) group in aldehydes and ketones.

Aldehydes and ketones also react with halogens, but in this case the halogen substitutes in the hydrocarbon portion of the molecule, e.g.

$$\underset{\text{acetaldehyde}}{CH_3 . CHO} + 3Cl_2 \rightarrow \underset{\text{chloral}}{CCl_3 . CHO} + 3HCl$$

General Reactions of Aldehydes NOT shown by Ketones

(*a*) *Oxidation.* Aldehydes are easily oxidized, whereas ketones are not.

$$R—C\begin{matrix}H\\=O\end{matrix} \rightarrow R—C\begin{matrix}OH\\=O\end{matrix} \text{ (i.e. R . COOH)}$$

Consequently, aldehydes are strong reducing agents. Thus—

(i) They reduce Fehling's solution and precipitate brownish-red cuprous oxide. Fehling's solution is made by adding a solution of copper sulphate to a solution of Rochelle salts—sodium potassium tartrate—and sodium hydroxide. The essential reaction with the aldehyde is—

$$2Cu(OH)_2 + R . CHO \rightarrow Cu_2O \downarrow + R . COOH + 2H_2O$$

(ii) They restore the pink colour to Schiff's reagent. Schiff's reagent is prepared by passing sulphur dioxide gas through an aqueous solution of rosaniline until the colour disappears.

(iii) They reduce ammoniacal silver nitrate solution to precipitate metallic silver. If the test is carried out under certain controlled conditions, the silver is deposited on the sides of the glass vessel in the form of a silver mirror.

(*b*) *Condensation Reaction.* Aldehydes react with themselves to form compounds known as *aldols* on adding a solution of potassium carbonate in the cold—

$$CH_3—CHO + CH_3—CHO \rightarrow \underset{\text{acetaldol}}{CH_3 . CH(OH) . CH_2 . CHO}$$

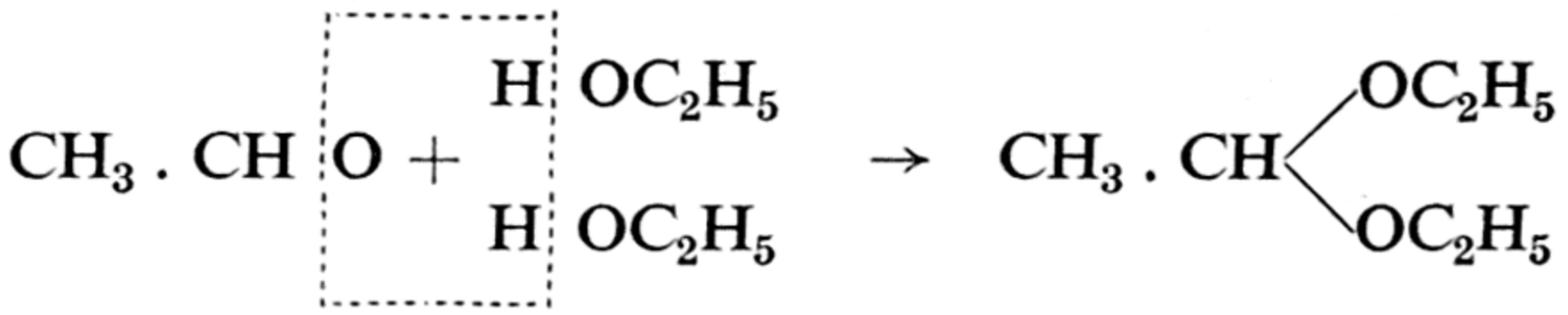
These aldols readily lose water on warming to form unsaturated aldehydes—

$$CH_3 . CH(OH) . CH_2 . CHO \rightarrow CH_3 . CH{=}CH.CHO$$

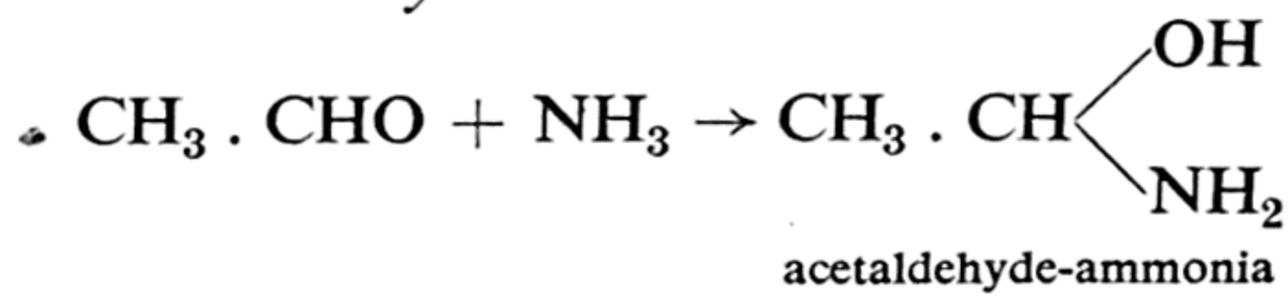
crotonaldehyde

A *condensation reaction* strictly speaking is a reaction in which two or more molecules react together to form a more complex molecule with the elimination of a molecule of water (or HCl, or other such simple molecule). The term, however, is also applied in the wider sense, as in the above aldol condensation, in which no water molecule is split off.

(*c*) Aldehydes react with alcohols on heating or in the presence of dissolved hydrogen chloride (which acts as a dehydrating agent) to form compounds known as *acetals*—



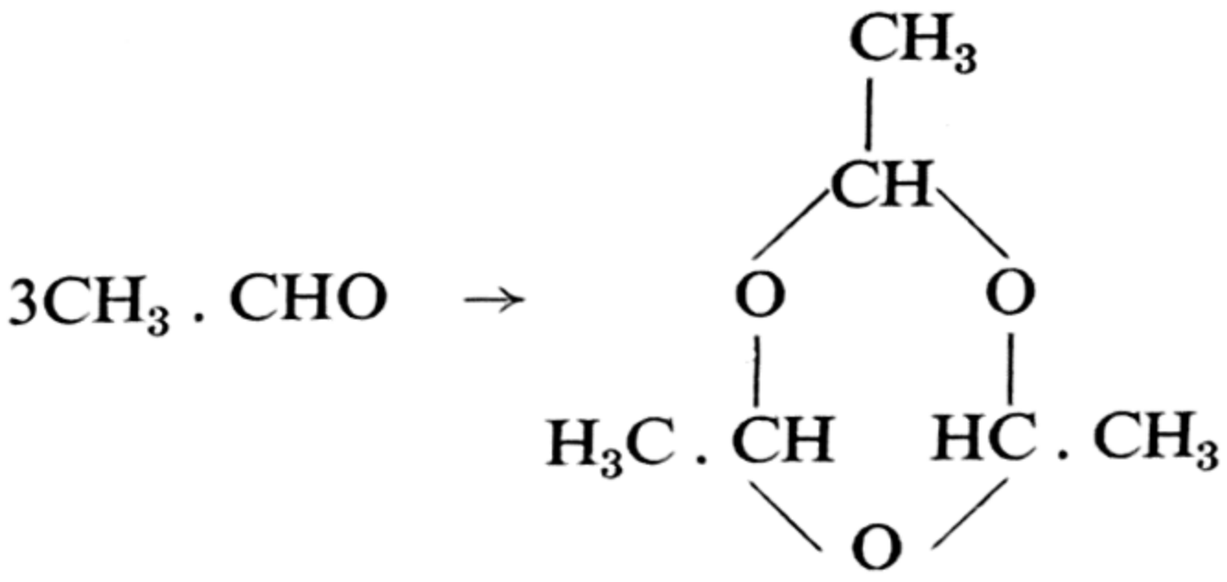
(*d*) Aliphatic aldehydes react with ammonia (anhydrous) to form compounds known as *aldehyde-ammonias*—



acetaldehyde-ammonia

Note, however, that formaldehyde gives *hexamine*, $(CH_2)_6N_4$, whilst ketones give complex condensation products.

(*e*) Aldehydes polymerize when treated with concentrated sulphuric acid. Thus acetaldehyde (b.p. 21°C) forms a polymer, known as *paraldehyde*, which is a colourless liquid boiling at 124°C.



paraldehyde

The polymer, known as *metaldehyde*, is formed when the polymerization occurs below 0°C. It is a white crystalline substance with the probable formula $(CH_3 . CHO)_4$.

(*f*) Aldehydes undergo a complex reaction to form brown resinous substances of doubtful composition on treatment with strong solutions of

sodium hydroxide. Formaldehyde, however, undergoes a different reaction to form sodium formate and methyl alcohol. This is an example of the Cannizzaro reaction—

$$2H\,.\,CHO + NaOH = H\,.\,COONa + CH_3OH$$

Mention may be made here of certain special reactions which occur with the *aromatic aldehydes*, such as benzaldehyde, $C_6H_5\,.\,CHO$, but not with aliphatic aldehydes, such as acetaldehyde—

(i) Cannizzaro's reaction with concentrated sodium hydroxide solution—

$$2C_6H_5\,.\,CHO + NaOH \rightarrow \underset{\text{sodium benzoate}}{C_6H_5\,.\,COONa} + \underset{\text{benzyl alcohol}}{C_6H_5\,.\,CH_2OH}$$

(ii) With ammonia, complex substances which are not aldehyde-ammonias are formed—

$$3C_6H_5\,.\,CHO + 2NH_3 \rightarrow (C_6H_5CH)_3N_2 + 3H_2O$$

(iii) With alcoholic potassium cyanide solution, the benzoin reaction occurs—

$$\begin{array}{l} C_6H_5\,.\,CHO \\ + \\ C_6H_5\,.\,CHO \end{array} \rightarrow \underset{\text{benzoin}}{\begin{array}{l} C_6H_5\,.\,CHOH \\ | \\ C_6H_5\,.\,C{=}O \end{array}}$$

(iv) With sodium acetate and acetic anhydride, cinnamic acids are formed by the so-called Perkin Synthesis—

$$C_6H_5\,.\,CHO + CH_3\,.\,COOH \rightarrow \underset{\text{cinnamic acid}}{C_6H_5\,.\,CH{=}CH\,.\,COOH}$$

THE ALDEHYDES

Formaldehyde, H . CHO. This industrially very important compound is prepared commercially by the catalytic oxidation of methyl alcohol vapour. A simple laboratory method for demonstrating this oxidation reaction is described on p. 894 in connexion with the properties of methyl alcohol. Commercially, however, a mixture of methyl alcohol vapour and air is passed through a reaction vessel packed with copper tubes containing rolls of silver or copper gauze at a temperature of 550°–600°C. The resulting formaldehyde is recovered from the issuing vapours by solution in water. Fractional distillation then produces the 37 per cent solution, known as *formalin*, which is sold commercially.

Increasing quantities of formaldehyde are also produced by the controlled oxidation of methane or natural gas from oil-wells.

Formaldehyde is a colourless gas with a very pungent, lachrymatory,

smell. It is very soluble in water, and also in alcohol and ether. Its most important industrial uses include—

(*a*) The manufacture of phenolic resins and plastics, such as Bakelite;

$$\text{Phenol } (C_6H_5OH) + \text{Formaldehyde} \rightarrow \text{Phenolic plastics}$$

(*b*) The manufacture of amino-resins and plastics, such as Beetle-ware;

$$\text{Urea } (CON_2H_4) + \text{Formaldehyde} \rightarrow \text{Amino-plastics}$$

(*c*) The manufacture of casein plastics, such as Erinoid and Lachmoid, due to a hardening action of the formaldehyde on the proteins present in casein.

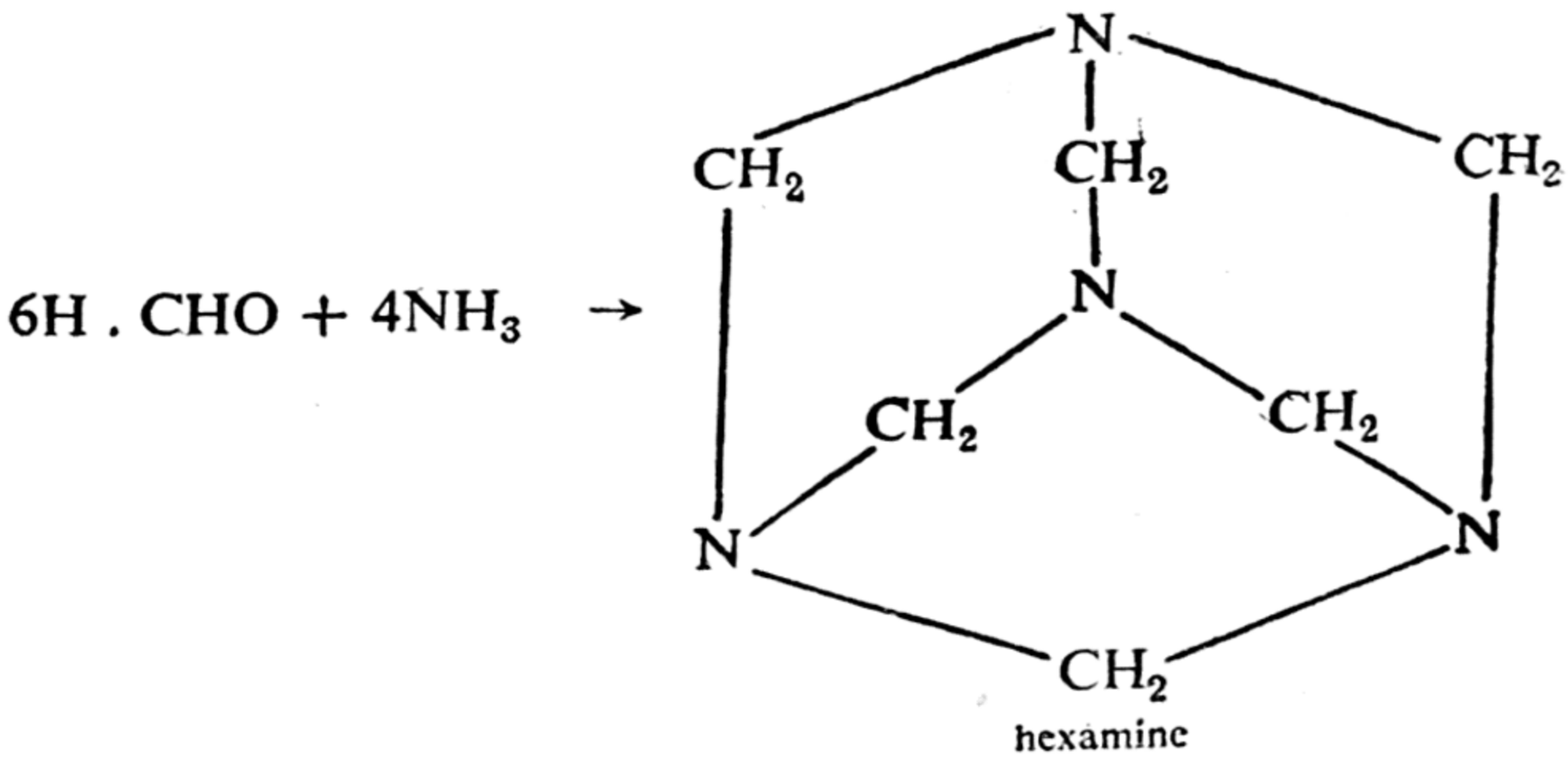
(*d*) The manufacture of the comparatively new high explosive known as R.D.X. or Cyclonite (*see* below).

(*e*) In the tanning industry to convert animal skins into leathers. Thus "doe-skin" leathers are produced, usually from sheep skins, by the action of formaldehyde.

(*f*) As an antiseptic and disinfectant. It is also used as a fungicide, for example, in the control of various fungi on farms, etc.

The reactions of formaldehyde are those already described on pp. 909–913, but the following are exceptional and should, therefore, be specially noted—

(i) With dry ammonia in ethereal solution, formaldehyde forms the complex compound, known as hexamethylene tetramine, or more concisely as hexamine, urotropine or aminoform.



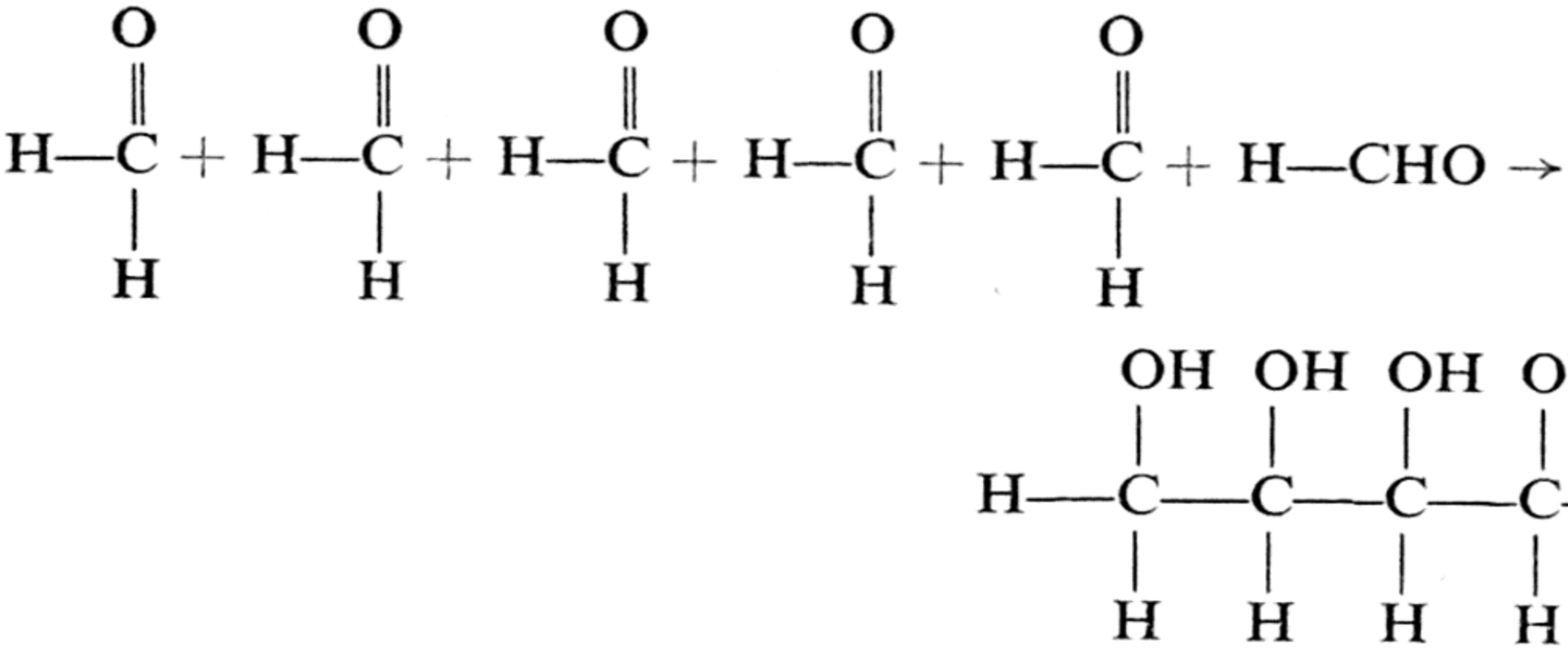
hexamine

This compound has certain medicinal uses. When nitrated it is converted into the explosive R.D.X. or Cyclonite.

(ii) With sodium hydroxide, instead of the usual aldehyde reaction to form a resin, formaldehyde undergoes a Cannizzaro reaction to form sodium formate and methyl alcohol—

$$2H \,.\, CHO + NaOH \rightarrow H \,.\, COONa + CH_3OH$$

(iii) Formaldehyde polymerizes in presence of lime-water, by means of an aldol condensation, to form a mixture of sugars, with the formula $C_6H_{12}O_6$, known as Formose.



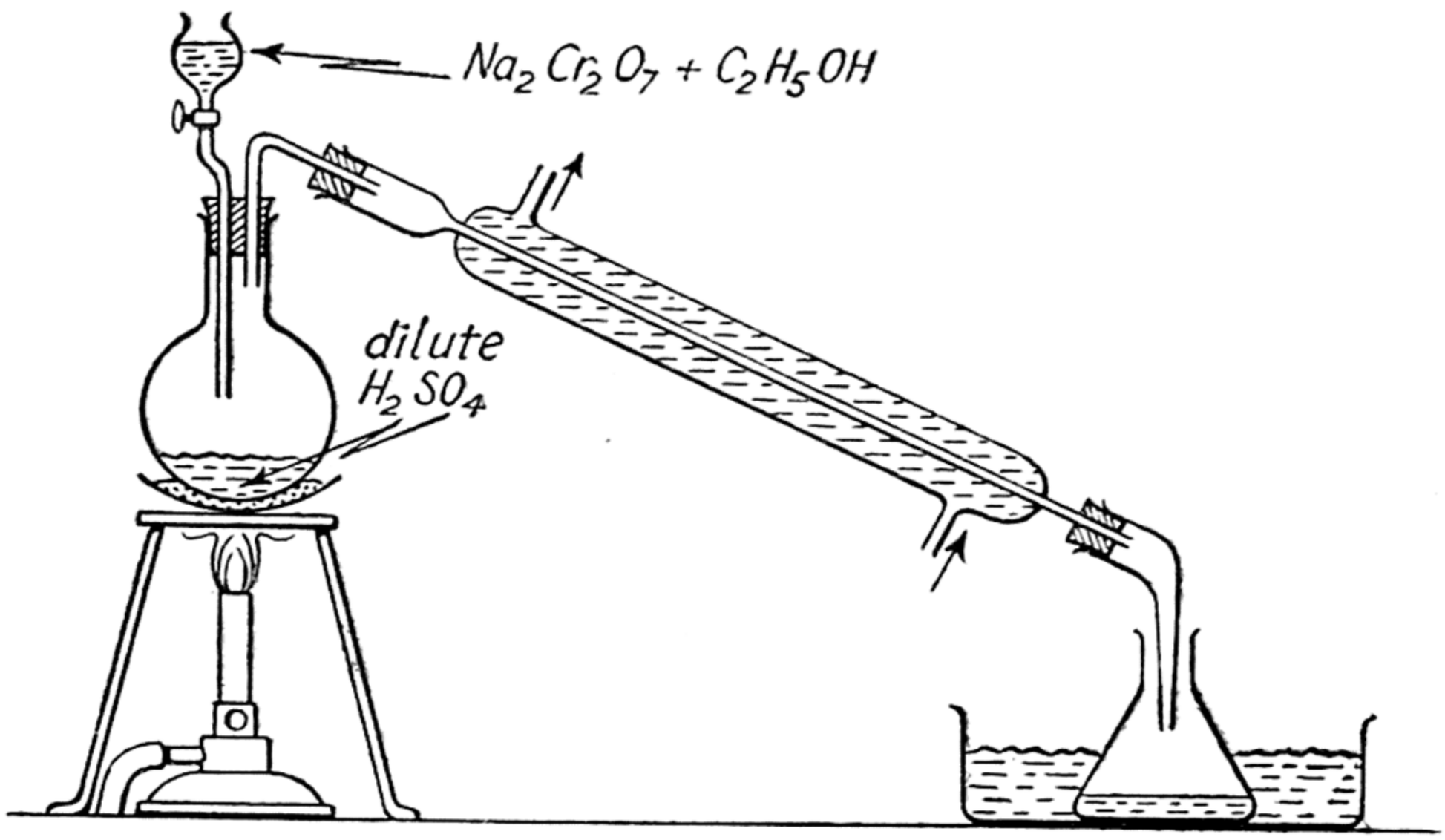


FIG. 264. Preparation of Acetaldehyde

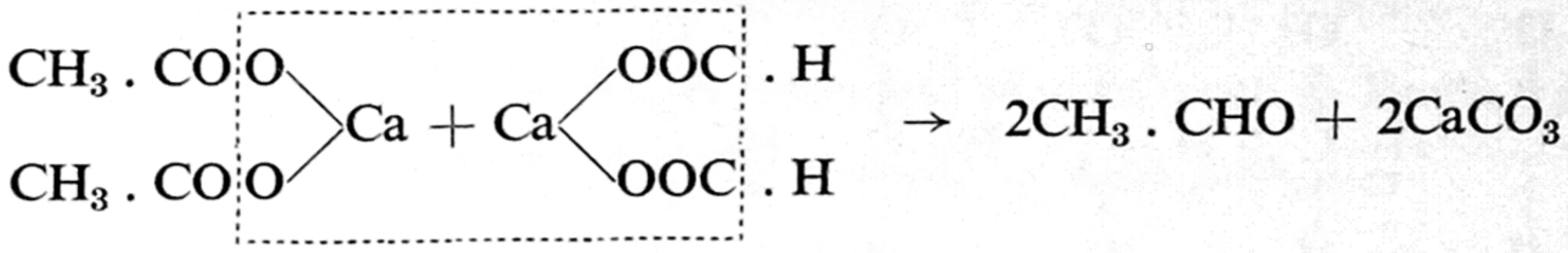
Acetaldehyde, CH_3 . CHO, may be prepared by the following methods.

1. By oxidizing ethyl alcohol with sodium or potassium dichromate and sulphuric acid. Since further oxidation of the acetaldehyde to acetic acid may occur, the procedure is to add a mixture of sodium dichromate and ethyl alcohol slowly to hot dilute sulphuric acid, as in the diagram above. Just sufficient of the dichromate-sulphuric acid mixture to oxidize the alcohol to the acetaldehyde stage is thus produced, and the latter distils off. In this way, the further oxidation to acetic acid is kept to a minimum

2. Better yields of acetaldehyde, however, are obtained by passing ethyl alcohol vapour over a finely divided copper catalyst at 250°–300°C.

$$C_2H_5OH \rightarrow CH_3 . CHO + H_2$$

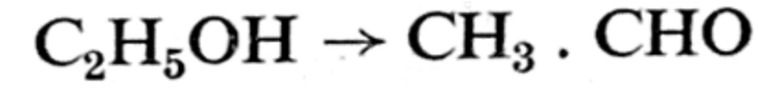
3. Acetaldehyde may also be produced by heating a solid mixture of calcium acetate and calcium formate, and condensing the acetaldehyde as in method (1) above.



Commercially, the most important methods are—

1. By passing acetylene into a suspension of mercurous sulphate in 25 per cent sulphuric acid under a pressure of about 15 lb/in.^{2} at a temperature between 70°–100°C, the latter being maintained by the heat of the reaction—

2. By passing ethyl alcohol vapour and air through a silver gauze catalyst at about 200°C. The following two reactions appear to occur simultaneously—



The acetaldehyde is recovered by solution in ethyl alcohol, from which it is later separated by distillation.

Acetaldehyde may be purified by treating the ethereal or alcoholic solution with dry ammonia gas. The crystals of acetaldehyde-ammonia which separate are removed, dried, and subsequently warmed with dilute sulphuric acid to liberate pure acetaldehyde.

Properties. Acetaldehyde is a colourless volatile liquid (boiling point 21°C) with a characteristic unpleasant smell. It is soluble in water, and also in alcohol and in ether.

Chemically, the reactions of acetaldehyde are mainly those already described in connexion with the general reactions of aldehydes and ketones on pp. 909–913. These reactions may be summarized as follows—

(*a*) *Reducing action*, as shown by (i) Fehling's solution, (ii) Schiff's reagent, and (iii) ammoniacal silver nitrate. In these reactions it is itself oxidized to acetic acid. The usual laboratory method, however, for oxidizing acetaldehyde to acetic acid is to heat with potassium dichromate and sulphuric acid.

(*b*) *When reduced*, for example, by passing acetaldehyde vapour and hydrogen over a finely divided nickel catalyst at about 200°C, it is converted to ethyl alcohol—

(*c*) *Addition reactions*, for example, with—

(i) saturated solution of sodium hydrogen sulphite to form a bisulphite compound. This is very soluble and rarely crystallizes.

(ii) hydroxylamine to form acetald-oxime, $CH_3 . CH{=}NOH$.

(iii) hydrazine to form (but not easily) the hydrazone

$$CH_3CH{=}N . NH_2$$

(iv) hydrogen cyanide to form the cyan-hydrin,

$$CH_3 . CH\begin{matrix}OH\\ \diagup\\ \diagdown\\ CN\end{matrix}$$

(v) anhydrous ammonia to form the acetaldehyde-ammonia

$$CH_3 . CH\begin{matrix}OH\\ \diagup\\ \diagdown\\ NH_2\end{matrix}$$

which reliberates acetaldehyde when warmed with dilute sulphuric acid.

(*d*) *Halogenation*

(i) with phosphorus pentachloride gives ethylidene dichloride—

$$CH_3 . CHO + PCl_5 \rightarrow CH_3 . CHCl_2 + POCl_3$$

(ii) with the halogens, substitution of the methyl group occurs slowly to give the mono-, di-, and eventually the tri-chloro-acetaldehyde, $CCl_3 . CHO$, known as chloral.

(*e*) *Condensation reactions*

(i) Aldol condensation. In the presence of a solution of potassium carbonate or very dilute caustic soda, two molecules of acetaldehyde combine to form acetaldol—

$$CH_3 . CHO + CH_3 . CHO \rightarrow CH_3 . CH(OH) . CH_2 . CHO$$

On warming this latter loses a molecule of water to form croton-aldehyde, $CH_3 . CH{=}CH . CHO$.

(ii) On heating acetaldehyde with ethyl alcohol at about 100°C, or by passing HCl gas into a mixture of these compounds and warming, reaction occurs to form acetal—

$$CH_3 . CH\begin{matrix}O\\ \\ H\\ H\end{matrix}\begin{matrix}+\\ \\ OEt\\ OEt\end{matrix} \rightarrow CH_3 . CH\begin{matrix}OEt\\ \diagup\\ \diagdown\\ Oet\end{matrix} + H_2O$$

(*f*) *Polymerization reactions*

(i) With a drop or two of concentrated sulphuric acid, heat is evolved and acetaldehyde polymerizes to form paraldehyde, $(CH_3 . CHO)_3$, a colourless liquid, boiling at 124°C. Paraldehyde shows none of the characteristic reactions of acetaldehyde. When warmed with dilute sulphuric acid, however, it reverts to acetaldehyde.

(ii) With acids at low temperatures (below 0°C), a different polymer, known as metaldehyde, is formed. This is a white crystalline solid, and under the name of "meta" is sold as a solid fuel. It is also used mixed with bran for killing slugs.

(iii) With strong solutions of caustic soda, acetaldehyde forms a brown resin, known as acetaldehyde resin.

Formula of Acetaldehyde. The molecular formula, C_2H_4O, is first determined by the usual steps involving (i) qualitative analysis, (ii) quantitative analysis and (iii) determination of the vapour density and hence molecular weight.

Reaction with PCl_5 gives the compound $C_2H_4Cl_2$. Since no HCl is evolved in this reaction, it follows that the oxygen is not present as a hydroxyl group.

The compound $C_2H_4Cl_2$ may be either

$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array} \qquad \text{or} \qquad \begin{array}{l} CH_3 \\ | \\ CHCl_2 \end{array}$$

A compound having the first of these two structures is obtained by the action of chlorine on ethylene. This suggests that the second, ethylidene dichloride, is formed from acetaldehyde.

Of the two possible formulae for acetaldehyde, namely—

$$\begin{array}{l} CH_2 \\ | \quad \diagdown \\ | \quad\ O \\ | \quad \diagup \\ CH_2 \end{array} \qquad \text{and} \qquad \begin{array}{l} CH_3 \\ | \\ CHO \end{array}$$

only the second would produce the compound

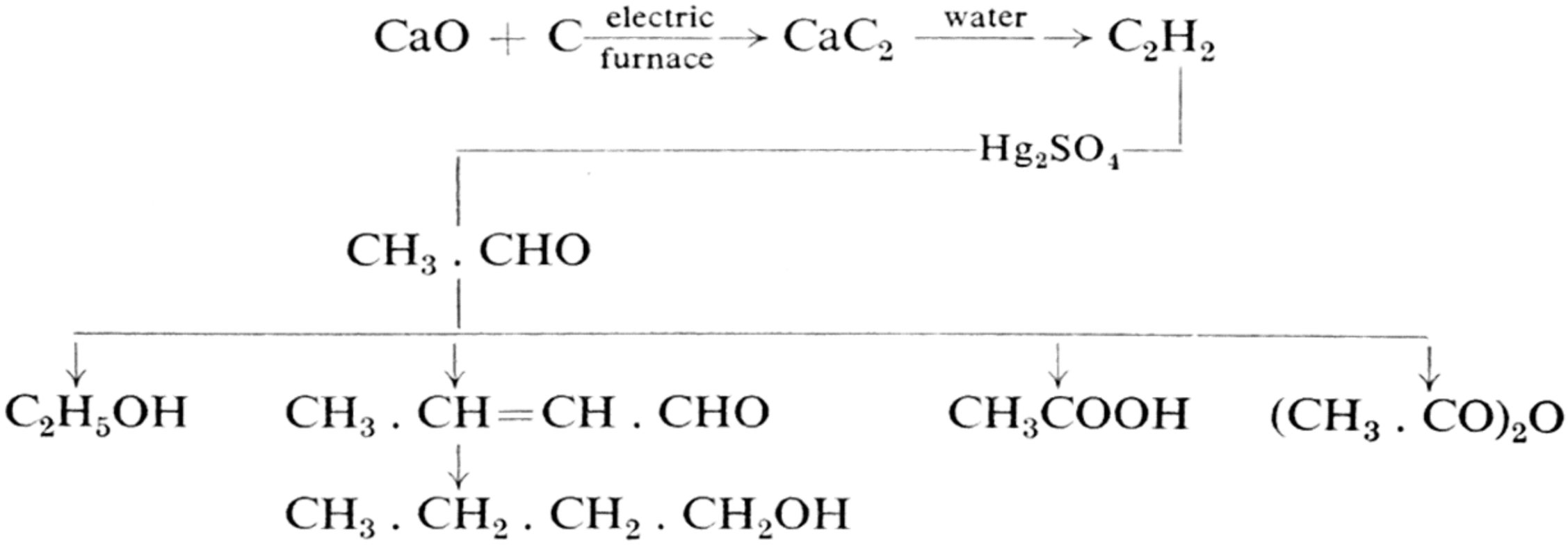
$$\begin{array}{l} CH_3 \\ | \\ CHCl_2 \end{array}$$

Acetaldehyde, therefore, has the structure

$$CH_3—C\begin{array}{l}\diagup H \\ \diagdown\!\!\diagdown O\end{array}$$

This formula is confirmed by the various reactions of acetaldehyde.

Uses of Acetaldehyde. Compounds such as ethyl alcohol, acetic acid, acetic anhydride, and butyl alcohol may easily be prepared from acetaldehyde. Since the latter may also easily be obtained indirectly from carbon (via acetylene), it follows that acetaldehyde forms an important link in the conversion of this abundant element into important organic compounds.

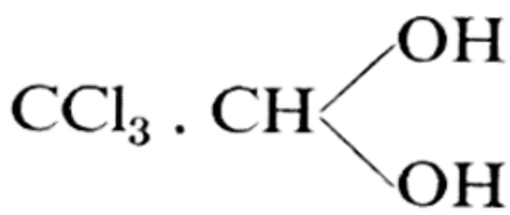


Chloral (or Trichloracetaldehyde), $CCl_3 . CHO$. This is obtained as a result of the direct action of chlorine on acetaldehyde, or more usually by the action of chlorine on ethyl alcohol. The ethyl alcohol is apparently first oxidized to acetaldehyde by the chlorine, and then combines with excess of the latter to form chloral.

$$C_2H_5OH \xrightarrow{Cl_2} CH_3 . CHO \xrightarrow{Cl_2} CCl_3 . CHO$$

It is an oily liquid, b.p. 97°C, and, since it retains the aldehyde (— CHO) group, it closely resembles acetaldehyde in its chemical properties. Two of its reactions, however, are particularly important—

(*a*) It combines with water to form a solid crystalline substance, known as chloral hydrate, $CCl_3 . CHO . H_2O$, with the structural formula



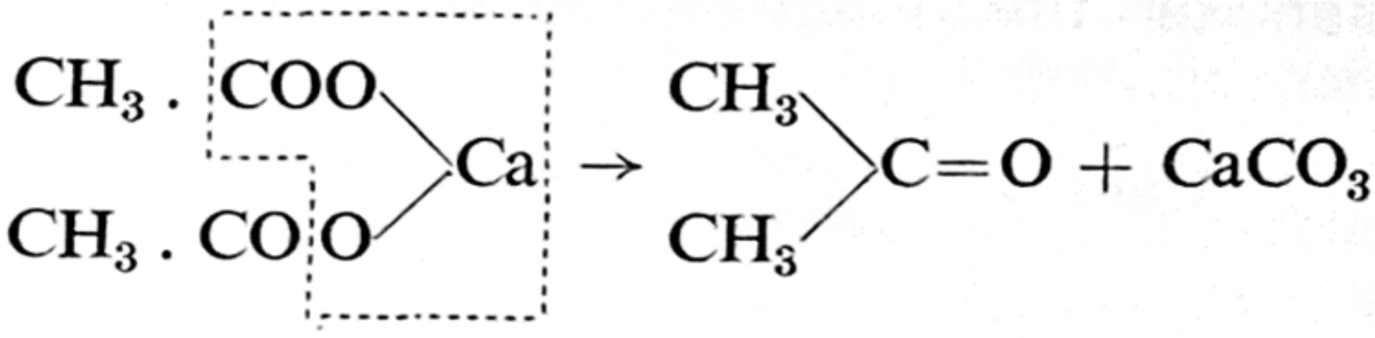
Chloral hydrate is one of the few examples of an organic compound in which two hydroxyl (— OH) groups are attached to the same carbon atom. The explanation of its stability appears to lie in the presence of the strongly electronegative chlorine atoms on the adjacent carbon atom. Chloral is used extensively in medicine as a soporific.

(*b*) When boiled with aqueous alkalis, chloral quickly hydrolyzes to form chloroform and sodium formate—

$$CCl_3 . CHO + NaOH \rightarrow CHCl_3 + H . COONa$$

KETONES

Acetone (or di-methyl ketone), $CH_3 . CO . CH_3$, is prepared in the laboratory by the dry distillation of calcium acetate. The latter is obtained commercially by neutralizing pyroligneous acid (obtained in the distillation of wood) with lime.



More recent industrial processes include—

(*a*) The interaction of ethyl alcohol and steam—

$$2C_2H_5OH + H_2O \rightarrow CH_3 . CO . CH_3 + 4H_2 + CO_2$$

Ethyl alcohol vapour mixed with a large excess of steam is passed through a temperature-controlled reaction vessel containing a mixed catalyst of iron and calcium acetate. The acetone is removed by condensation and washing, and is eventually concentrated by fractional distillation.

(*b*) In the U.S.A. increasing quantities of acetone are produced indirectly from propylene, which is a by-product of the manufacture of petrol by cracking. The propylene is converted into isopropyl alcohol by reaction with sulphuric acid—

$$CH_3 . CH{=}CH_2 + H_2O \rightarrow CH_3 . CH(OH) . CH_3$$

The isopropyl alcohol is then converted into acetone by passing the vapour over a copper gauze catalyst at 300°C.

$$CH_3 . CH(OH) . CH_3 \rightarrow CH_3 . CO . CH_3 + H_2$$

(*c*) Acetone is also produced by the bacterial fermentation of maize, and other starchy materials, and more recently of molasses. Special selected strains of bacteria have been developed which ferment sugars to acetone and butyl alcohol. After each batch fermentation, the vessels are carefully sterilized to destroy unwanted micro-organisms which grow during the fermentation process and which have different actions on the sugars. The Weizmann bacteria (so-called after their discoverer) are carefully grown in the laboratory, and used to inoculate each fresh batch ready for fermentation.

Properties of Acetone. Acetone is a colourless liquid (b.p. 56·5°C) and has a peculiar pleasant odour. It is soluble in water, alcohol, ether, etc., and is itself an extremely important solvent for other organic compounds.

Chemically its reactions are mainly those already described on page 910.

(*a*) Unlike acetaldehyde it is not a reducing agent, although it slowly

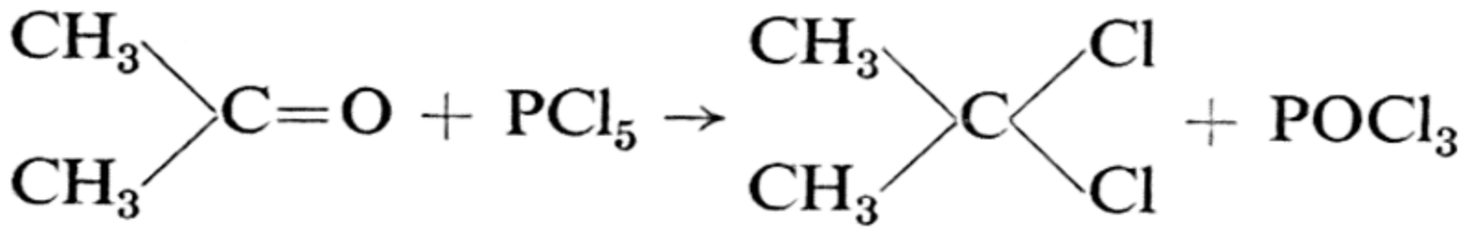
restores the colour to Schiff's reagent. With strong oxidizing agents, disruption of the molecule occurs to form acetic acid, carbon dioxide and water—

$$(CH_3)_2C{=}O + 4\bar{O} \rightarrow CH_3 \,.\, COOH + CO_2 + H_2O$$

(*b*) Reduction with nascent hydrogen, or vapour phase reduction over a nickel catalyst, produces isopropyl alcohol, $CH_3 \,.\, CH(OH) \,.\, CH_3$

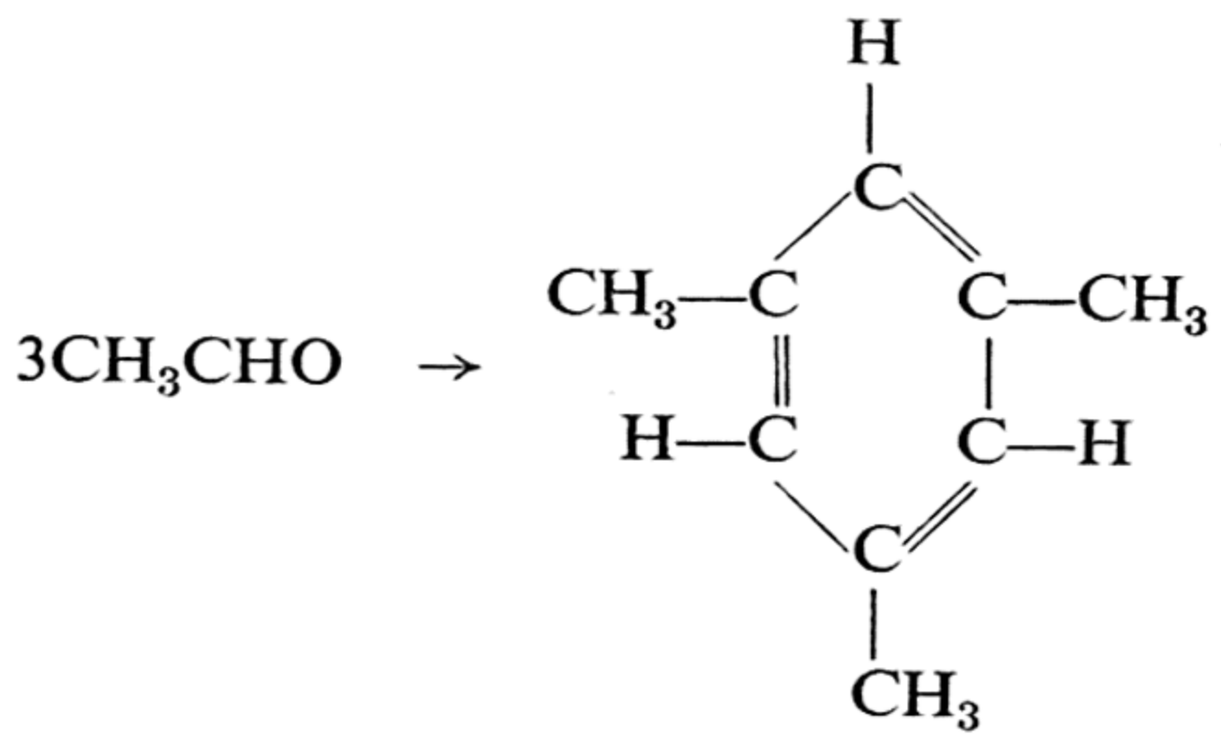
(*c*) *Addition Reactions.* Acetone forms a white precipitate of a bisulphite compound with a concentrated solution of sodium bisulphite; an oxime with hydroxylamine; a hydrazone with hydrazine or phenyl hydrazine; and a cyan-hydrin with hydrogen cyanide.

(*d*) *Halogenation.* Phosphorus halides (such as PCl_5) replace the carbonyl oxygen with two halogen atoms—



Reaction with the halogens, however, leads to substitution of the hydrogen atoms to form, for example, trichloro-acetone $CCl_3 \,.\, CO \,.\, CH_3$.

(*e*) *Condensation Reactions.* The most important of these occurs on heating acetone with concentrated sulphuric acid. Three molecules combine together with elimination of three molecules of water to form an aromatic hydrocarbon, known as mesitylene (or trimethyl-benzene)—



(*f*) Acetone resembles acetaldehyde and ethyl alcohol in undergoing the iodoform reaction (*see* p. 890).

Uses of Acetone. Acetone is one of the most powerful solvents known. It is used in this connexion, for example, in the manufacture of cellulose acetate rayon and cellulose acetate dope, in the manufacture of varnishes and paints, in the manufacture of cordite from nitrocotton and nitroglycerine, in the "graining" of tetryl explosive, and in the liquid state for the storage and transport of acetylene. Chemically, it is used in the manufacture of chloroform, iodoform, sulphonal, and various intermediates in the manufacture of synthetic rubber.

Formula. It may be shown by the usual methods, enumerated for acetaldehyde, that acetone has the formula, C_3H_6O. Since the oxygen is not present as a hydroxyl (—OH) group, as shown by the non-liberation of HCl when it is reacted with phosphorus pentachloride, the only possible formulae appear to be—

$CH_3 . CO . CH_3$ (*a*) $\quad CH_3 . CH_2 . CHO$ (*b*) or $CH_3 . CH{-}CH_2$ (*c*), with O bridging the CH and CH_2 groups

Formula (*b*) is that of an aldehyde and hence cannot apply to acetone. The reaction with PCl_5 in which both the halogen atoms are introduced on the middle carbon atom rules out formula (*c*) since this latter would give the unsymmetrical compound, $CH_3 . CHCl . CH_2Cl$. The formula of acetone is therefore

$O{=}C(CH_3)_2$

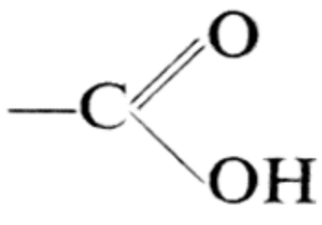
CHAPTER 32

FATTY ACIDS AND THEIR DERIVATIVES

THE aliphatic monobasic acids or fatty acids are the ultimate oxidation products of alcohols, aldehydes and ketones—

$$R . CH_2OH \rightarrow R . CHO \rightarrow R . COOH$$

They form a typical homologous series with the general formula $C_nH_{2n+1} . COOH$. The characteristic acid group is the carboxyl (—COOH) group, which may more correctly be written as



In this group the carbonyl group causes the hydroxylic hydrogen to become acidic. It is this hydrogen which is replaced by metals to form salts and which is ionized on solution in water—

$$CH_3 . COOH \rightleftharpoons (CH_3 . COO)^- + H^+$$

It may be pointed out at this stage that certain other groups may also enhance the acidity of the hydroxylic hydrogen, one simple example being found in the phenols (*see* p. 994) in which the hydroxyl is attached to the aromatic phenyl group. These are not however as strongly acidic as the fatty acids, so that the effect of the phenyl group, although considerably greater than that of any alkyl radical, is less than that of the carbonyl (C=O) group.

$$CH_3OH \qquad C_6H_5OH \qquad CH_3 . COOH$$

$$\longrightarrow \text{increasing acidity} \longrightarrow$$

In the table on p. 924 are given the names, formulae and melting points of the more familiar fatty acids.

General Methods of Preparation

1. By oxidation of alcohols, aldehydes and ketones—

Primary Alcohol

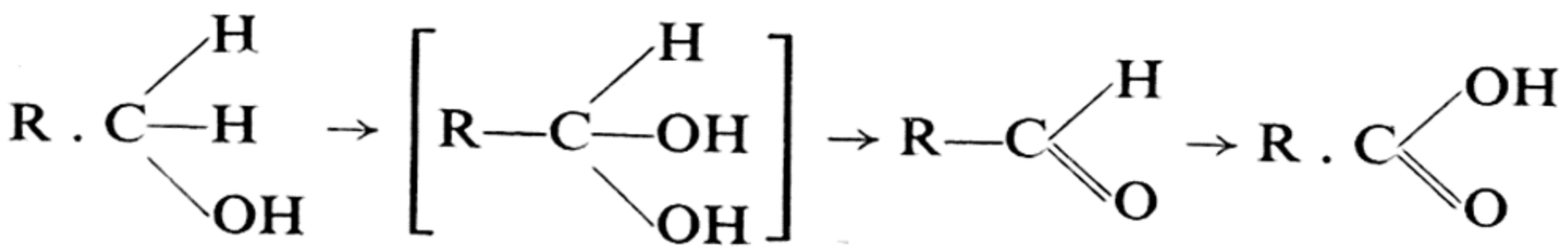
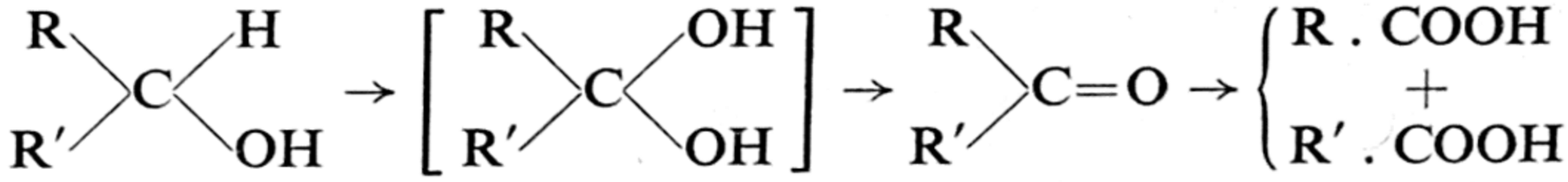


TABLE 117

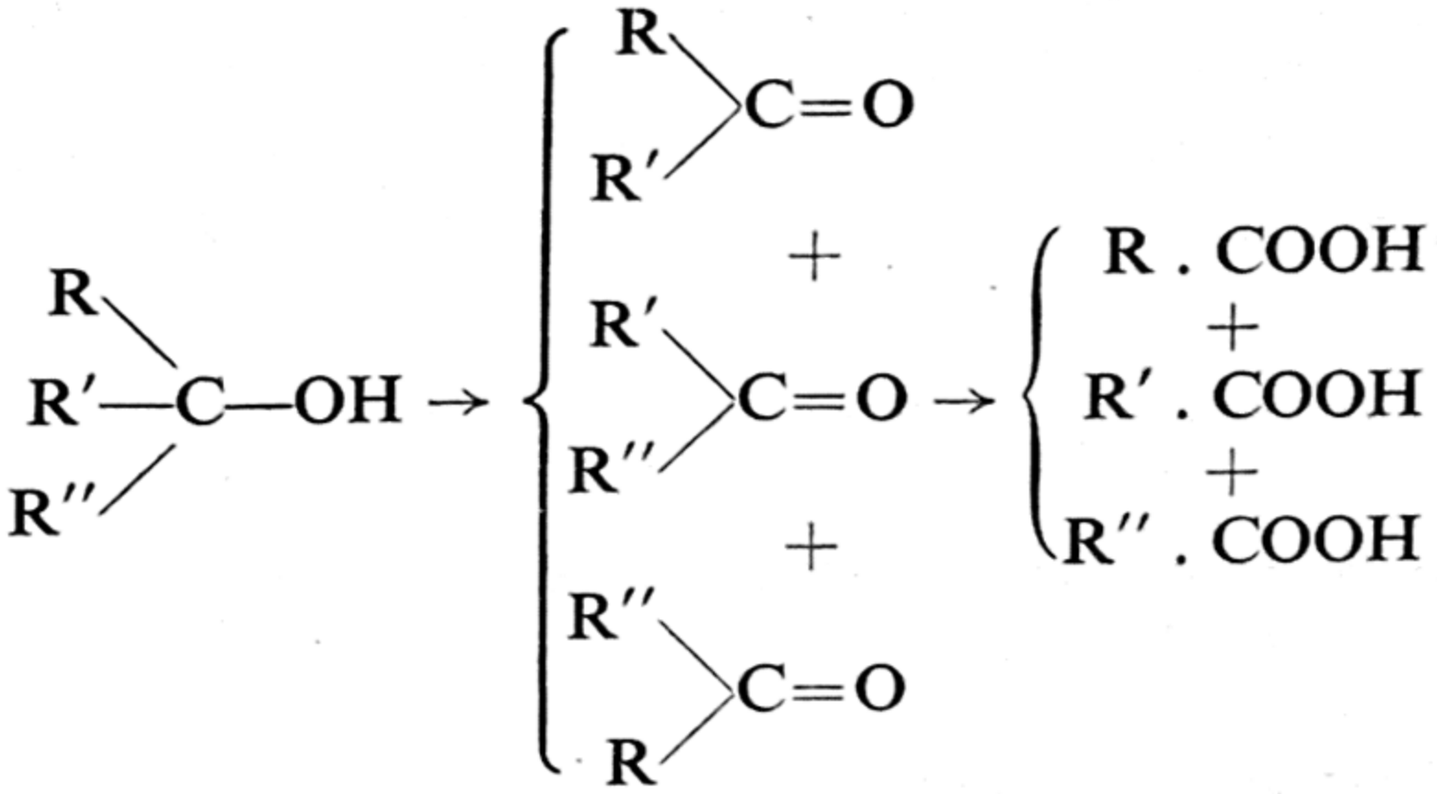
Some Common Fatty Acids

Fatty Acid	Formula	M.P. (°C)	B.P. (°C)
Formic acid . . .	H . COOH	8·3	101
Acetic acid	CH_3 . COOH	16·7	118
Propionic acid . . .	C_2H_5 . COOH	— 36·0	140
n-Butyric acid . . .	C_3H_7 . COOH	— 8·0	162
iso-Butyric acid . . .	C_3H_7 . COOH	— 79·0	155
n-Valeric acid . . .	C_4H_9 . COOH	— 59·0	186
iso-Valeric acid . . .	C_4H_9 . COOH	— 51·0	174
Lauric acid . . .	$C_{11}H_{23}$. COOH	+ 44·0	
Myristic acid . . .	$C_{13}H_{27}$. COOH	+ 54·0	
Palmitic acid . . .	$C_{15}H_{31}$. COOH	+ 63·0	
Stearic acid . . .	$C_{17}H_{35}$. COOH	+ 71·0	

Secondary Alcohol



Tertiary Alcohols



Note. Those reactions in which disruption of the molecule occurs to form compounds containing fewer carbon atoms only occur with very strong oxidizing agents; that is, they only occur with difficulty. The other oxidation reactions occur easily, and are often effected in the laboratory by warming with potassium dichromate and dilute sulphuric acid.

2. By hydrolysis of the alkyl cyanides (or nitriles) by boiling with dilute mineral acids or alkalis. It will be recalled that these cyanides are prepared

most easily from the corresponding alkyl iodide by treatment with potassium cyanide in alcoholic solution—

$$R—I + KCN \rightarrow R—CN + KI$$

$$R—C\equiv N \rightarrow R—C(OH)(=NH) \rightarrow R—C(OH)_2(OH)(NH_2) \rightarrow R—C(=O)(OH) + NH_3$$

3. By hydrolysis (saponification) of esters. This method, as exemplified by—

$$R\,.\,COOC_2H_5 + H_2O \rightarrow R\,.\,COOH + C_2H_5OH$$

is important for the higher acids (palmitic, stearic, etc.) which occur as their glyceryl esters in many fats and waxes found in nature.

General Properties and Reactions

To understand the way in which the physical properties of the members of this series vary with increase in their molecular weight, it should be realized that each acid is composed essentially of a hydrocarbon portion (C_nH_{2n+1}—) and a carboxyl portion (—COOH).

In the earlier members, the influence of the carboxyl group is predominant. They are colourless liquids, soluble in water, alcohol and ether, are acids, and have each a pronounced and characteristic odour. With increase in molecular weight, the hydrocarbon portion increases in size, and so has an increasingly greater say in the properties of the molecule as a whole. Thus the intermediate members are colourless *oils*, only sparingly soluble in water (but still soluble in alcohol and ether), and have a much less pronounced and more rancid odour. The peculiar odour, for example, of rancid butter is due to the presence of butyric acid. With further increase in molecular weight, the acids become *wax-like solids*, insoluble in water and with little if any smell. The increasing hydrocarbon-like character also reveals itself in a progressive decrease in density from 1·24 for formic acid to 0·85 for stearic acid (paraffin wax has a density of 0·8–0·9), and increasing inflammability. Thus, stearic acid, $C_{17}H_{35}\,.\,COOH$ is a white waxy solid which is used in the manufacture of high quality candles.

Chemically, the general reactivity associated with the carboxyl (—COOH) group diminishes with increase in molecular weight. Indeed, in the highest acids, their essentially acidic character is only revealed by such reactions as the formation of salts with alkalis. With this reservation, the general reactions of the aliphatic monobasic acids may be summarized as follows—

1. Normal acid reaction with bases and alkalis to form salts

$$R\,.\,COOH + NaOH \rightarrow R\,.\,COONa + H_2O$$

2. Formation of *esters* with alcohols in the presence of a dehydrating

agent such as concentrated sulphuric acid, anhydrous zinc chloride or dissolved hydrogen chloride. Unlike the previous reaction, this is a typically organic (i.e. covalent) reaction. It occurs slowly, the rate being increased by increasing the temperature.

$$R\,.\,CO\,|OH + H|\,OC_2H_5 \rightarrow R\,.\,COOC_2H_5 + H_2O$$

3. Formation of *acyl chlorides* (in which the —OH is replaced by —Cl) by the action of phosphorus chlorides (PCl_5, PCl_3, or $POCl_3$).

$$R\,.\,C(=O)OH + PCl_5 \rightarrow R\,.\,C(=O)Cl + POCl_3 + HCl$$

Note. These reactions are carried out with the anhydrous acid under water free conditions.

4. If it is required to introduce the halogen into the hydrocarbon portion of the molecule, the halogen itself is used. Reaction occurs, for example, on passing chlorine into the hot solution of the acid to produce various substitution products. Thus acetic acid is ultimately converted into trichlor-acetic acid, $CCl_3\,.\,COOH$—

$$CH_3\,.\,COOH \rightarrow CH_2Cl\,.\,COOH \rightarrow CHCl_2\,.\,COOH \rightarrow CCl_3\,.\,COOH$$

5. Formation of *acid anhydride* when the anhydrous acid is heated with a dehydrating agent, such as, phosphorus pentoxide—

$$\begin{matrix} R\,.\,CO|OH| \\ + \\ R\,.\,COO|H| \end{matrix} \rightarrow \begin{matrix} R\,.\,CO \\ \\ R\,.\,CO \end{matrix}\!\!>\!O + H_2O$$

6. Formation of a *hydrocarbon* on heating a mixture of the sodium salt (or acid) with soda-lime (e.g. preparation of methane from sodium acetate)—

$$R\,.\,COONa + NaOH \rightarrow R\,.\,H + Na_2CO_3$$

7. Formation of a higher *hydrocarbon* by the electrolysis of a concentrated solution of a salt of the acid, the hydrocarbon being liberated at the anode—

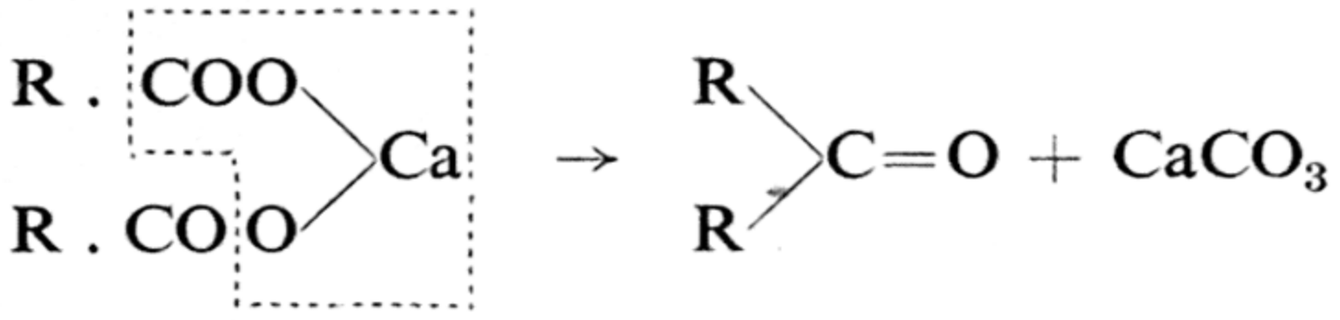
$$R\,.\,COOK\ (\text{ionization}) \rightleftharpoons (R\,.\,COO)^- + K^+$$

Anode reaction

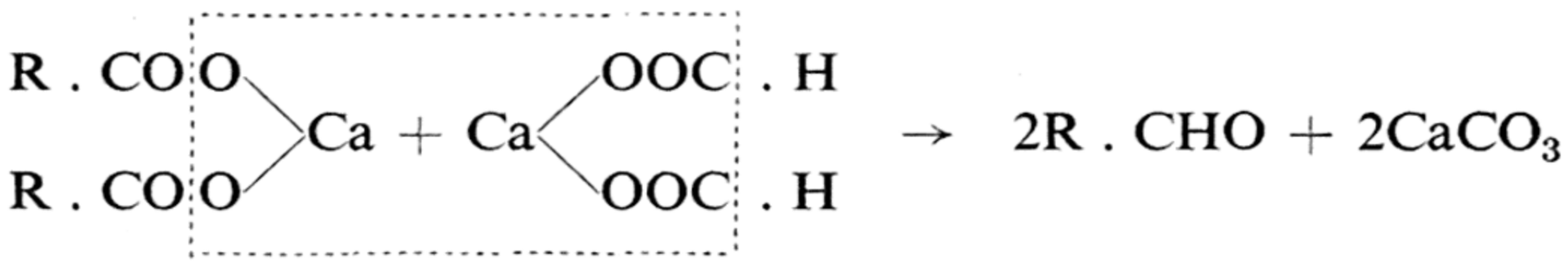
$$(R\,.\,COO)^- \rightarrow (R\,.\,COO) \rightarrow (R) + CO_2$$

followed immediately by $2(R) \rightarrow R—R$

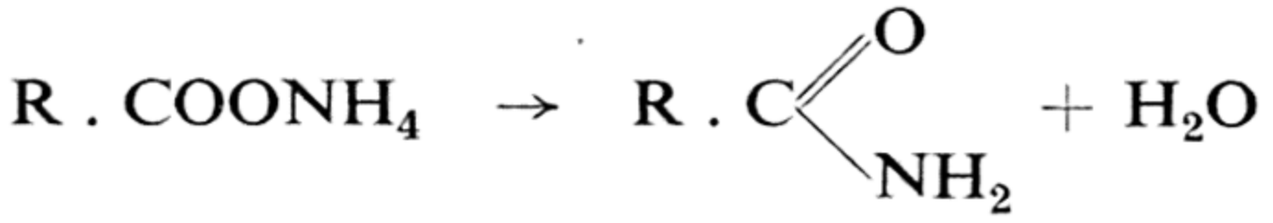
8. Formation of *ketone* on distilling the calcium salt alone—



9. Formation of *aldehyde* on distilling an equimolecular mixture of the calcium salt with calcium formate—



10. Formation of an *amide* ($R . CONH_2$) on heating the ammonium salt—



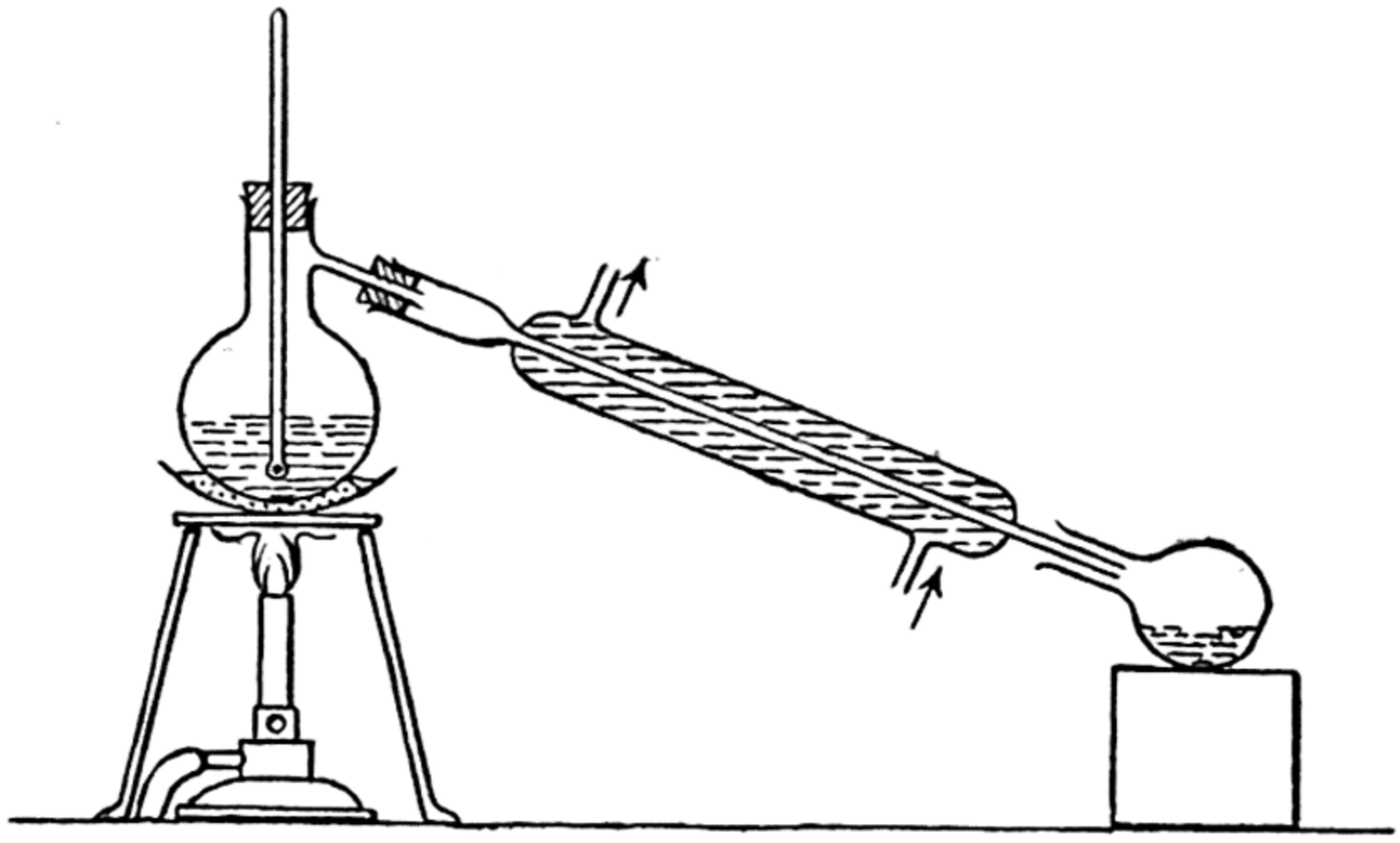


FIG. 265. Preparation of Formic Acid from Oxalic Acid

Further heating in presence of a strong dehydrating agent such as phosphorus pentoxide converts the amide into the corresponding cyanide—

$$R . CONH_2 - H_2O \rightarrow R . CN$$

Formic Acid, H . COOH. This is the first member of the series and may be prepared by the following methods—

1. The usual laboratory method is to heat a mixture of *anhydrous* glycerol and oxalic acid crystals ($H_2C_2O_4 . 2H_2O$) in the apparatus as shown in the diagram (Fig. 265).

The net result, as far as the oxalic acid is concerned, is represented by the equation—

$$\begin{matrix}COOH\\|\\COOH\end{matrix} \rightarrow H\,.\,COOH + CO_2$$

Aqueous formic acid distils over and is condensed and collected. The actual stages in the reaction are, however, somewhat more complex than the above simple equation suggests. Thus, the first stage appears to be the formation of the ester, glyceryl monoxalate—

$$\begin{matrix}CH_2O\boxed{H} + \boxed{HO}OC\,.\,COOH\\|\\CHOH\\|\\CH_2OH\end{matrix} \rightarrow \begin{matrix}CH_2OOC\,.\,COOH\\|\\CHOH\\|\\CH_2OH\end{matrix} + H_2O\,.$$

At about 100°C, this ester decomposes to form the corresponding formic acid ester, namely, glyceryl monoformate—

$$\begin{matrix}CH_2OOC\,.\,\boxed{COO}\boxed{H}\\|\\CHOH\\|\\CH_2OH\end{matrix} \rightarrow \begin{matrix}CH_2OOC\,.\,H\\|\\CHOH\\|\\CH_2OH\end{matrix} + CO_2$$

On further heating, especially if fresh oxalic acid crystals be added at this stage, hydrolysis occurs to liberate formic acid and reform the glycerol. The necessary water for this hydrolysis is provided by the first reaction and by the water of crystallization present in the oxalic acid crystals.

$$\begin{matrix}CH_2\boxed{OOC\,.\,H} + \boxed{H-}\boxed{-OH}\\|\\CHOH\\|\\CH_2OH\end{matrix} \rightarrow \begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix} + H\,.\,COOH$$

2. An aqueous solution of formic acid may also be obtained by heating methyl alcohol with excess of potassium dichromate and dilute sulphuric acid, and collecting the distillate.

$$CH_3OH \rightarrow H\,.\,CHO \rightarrow H\,.\,COOH$$

3. Formic acid is prepared commercially by the reaction—

$$NaOH + CO \rightarrow H\,.\,COONa$$

sodium formate

The carbon monoxide (for example, from producer gas) is passed under 8–10 atmospheres pressure over sodium hydroxide at about 200°C. The resulting sodium formate is then acidified and the formic acid distillate collected.

In this reaction, it should be noted that carbon monoxide is behaving as an acidic oxide. This is confirmed by—

(*a*) The formation of small quantities of formic acid when a silent electric discharge is passed through a mixture of carbon monoxide and steam.

(*b*) The liberation of carbon monoxide when formic acid is dehydrated with concentrated sulphuric acid.

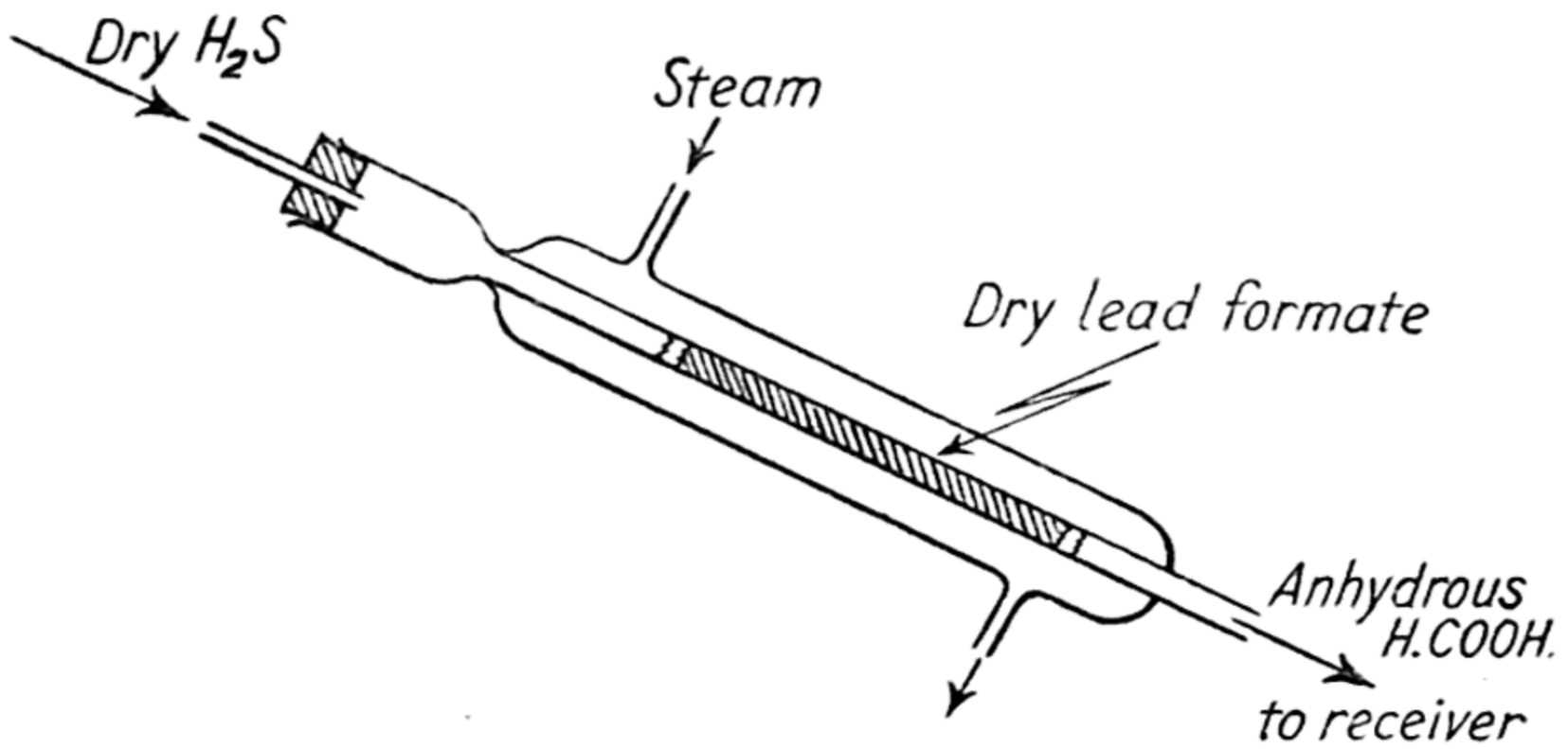


FIG. 266. Preparation of Anhydrous Formic Acid from Lead Formate

Preparation of Anhydrous Formic Acid. The stages in the production of anhydrous formic acid from its aqueous solutions are—

(*a*) Treatment with powdered lead carbonate to convert the formic acid to lead formate

$$2H\,.\,COOH + PbCO_3 \rightarrow (H\,.\,COO)_2Pb + H_2O + CO_2$$

The reaction is completed by stirring and warming until no further effervescence due to carbon dioxide is observed.

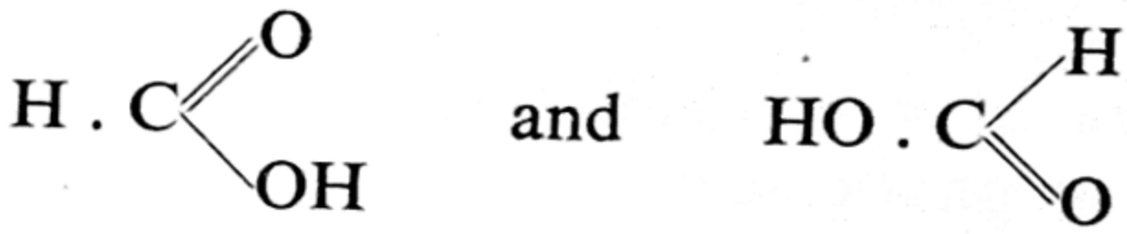
(*b*) The solution of lead formate obtained on boiling is filtered hot to separate unchanged lead carbonate, and the clear filtrate then allowed to cool to produce colourless crystals of lead formate. These are filtered off, washed and dried.

(*c*) Since lead formate crystals do not contain water of crystallization, they may be decomposed by the action of dry sulphuretted hydrogen to liberate the pure anhydrous formic acid.

$$(H\,.\,COO)_2Pb + H_2S \rightarrow PbS + 2H\,.\,COOH$$

Properties of Formic Acid. Formic acid is a colourless liquid with a pungent irritating smell. It produces blisters on the skin, and is in fact

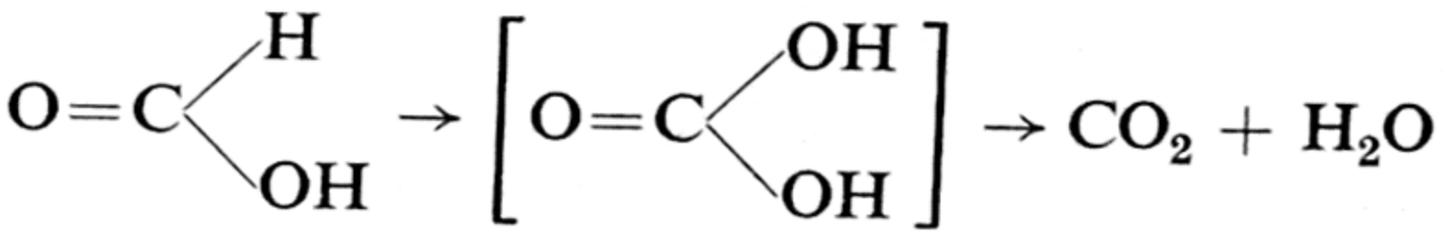
present in the stings of bees and ants and also in the stinging-nettle plants. The original isolation of formic acid by distilling red ants explains its name which is derived from the latin word for an ant, namely *formica*. Chemically, it differs in many of its reactions from those of acetic acid and the other acids of the series. These differences are due to the fact that in addition to being an acid, formic acid is also an aldehyde. This dual role is readily seen by studying for a moment the following two ways of writing the structural formula



These two formulae are, of course, identical.

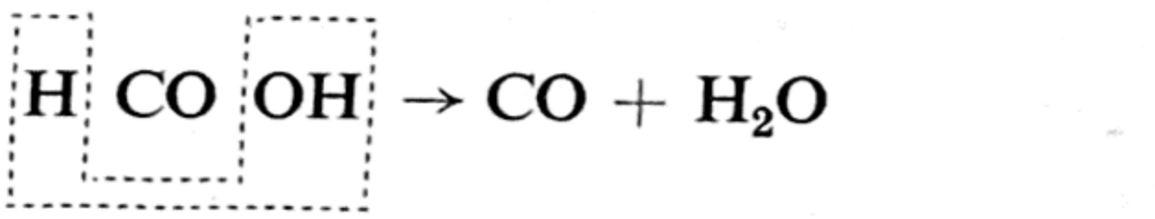
The principal reactions of formic acid and its salts are as follows—

1. It is easily oxidized and hence is a strong reducing agent (like formaldehyde)—



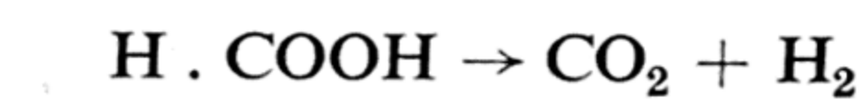
Thus, formic acid reduces ammoniacal silver nitrate to give the silver mirror test, and Fehling's solution to give a precipitate of cuprous oxide.

2. When warmed with concentrated sulphuric acid, the latter removes the elements of water from the formic acid to liberate carbon monoxide gas.

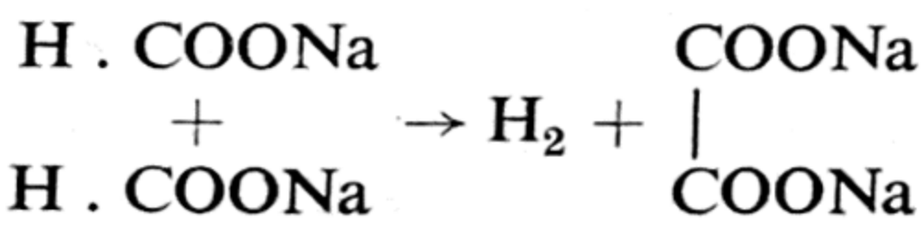


The reaction may conveniently be carried out in a test-tube and the issuing carbon monoxide ignited. If the reaction is sufficiently vigorous, the carbon monoxide will continue to burn with a characteristic blue flame.

3. When heated alone, for example at about 160°C in closed vessels, formic acid decomposes to form carbon dioxide and hydrogen



4. When the sodium and potassium salts are heated, hydrogen is liberated and the corresponding oxalates formed—



5. Ammonium formate heated alone loses a molecule of water to produce formamide, and this on further heating with phosphorus pentoxide is converted to hydrogen cyanide—

$$H\,.\,COONH_4 \rightarrow H\,.\,CONH_2 \rightarrow HCN$$

6. Formic acid, unlike acetic acid, does not form an anhydride; and with phosphorus pentachloride hydrogen chloride and carbon monoxide are formed, presumably through the intermediate formation of an unstable formyl chloride—

$$H\,.\,COOH\,(+\,PCl_5) \rightarrow \left[H\,.\,C\begin{matrix}=O\\ \diagdown\\ \diagup\\ -Cl\end{matrix}\right] \rightarrow HCl + CO$$

Compared with the other fatty acids, formic acid is also a much stronger acid. This enhanced acidity results from the replacement of the alkyl group by a hydrogen atom—

$$CH_3\,.\,COOH\ (\text{very weak acid}) \rightarrow H\,.\,COOH\ (\text{acid})$$

Acetic Acid, $CH_3\,.\,COOH$. This industrially very important chemical was formerly prepared commercially from pyroligneous acid, but nowadays the bulk of the acetic acid required by industry is produced synthetically from acetylene or by oxidation of ethyl alcohol. Dilute solutions are still, however, produced by the fermentation (vinegar) process, but even this time-honoured process has been improved to increase the rate of formation of acetic acid.

From Pyroligneous Acid. The pyroligneous acid obtained by the dry distillation of wood is treated with milk of lime to convert the acetic acid into calcium acetate. The solution is then evaporated to remove the volatile compounds (acetone, methyl alcohol, etc.) and the residue of calcium acetate then distilled with concentrated hydrochloric acid. The aqueous distillate of acetic acid is then redistilled with concentrated sulphuric acid to give the anhydrous (*glacial*) acetic acid.

From Acetylene. Acetaldehyde is first formed from acetylene by the mercurous sulphate/sulphuric acid method described on page 916—

$$C_2H_2 + H_2O \rightarrow CH_3\,.\,CHO$$

The solution of acetaldehyde, so obtained, is then oxidized by air at about 55°C in the presence of about 0·1 per cent of manganese acetate which acts as a catalyst and also helps to prevent the formation of explosive peracetic acid—

$$CH_3\,.\,CHO \rightarrow CH_3\,.\,COOH$$

The acetic acid is then recovered by distillation and rectified to produce the glacial acid.

From Ethyl Alcohol. The alcohol is first oxidized catalytically in the

vapour phase to acetaldehyde (*see* p. 915), and the resulting acetaldehyde vapour then mixed with more air and passed into a 95 per cent solution of acetic acid where the final stage, the oxidation of the acetaldehyde to acetic acid, occurs.

Fermentation Process.. In the old method alcoholic solutions, such as poor quality wines, ciders and beers, were allowed to stand in contact with the air, when bacterial oxidation slowly occurred to form "vinegar" containing about 5 per cent of acetic acid. In the present-day *quick-vinegar process*, the time of this bacterial oxidation is reduced from a period of months to one of days. The dilute alcoholic solution, usually mixed with vinegar, is allowed to trickle down tall wooden tanks packed with beech-wood shavings or birch twigs, which have been treated with the particular *bacterium aceti* culture which ferments the alcohol to acetic acid. A plentiful supply of air is necessary, since the process is essentially one of oxidation involving enzymes present in the *bacterium aceti* spores. The liquid passing through the tanks is continuously recirculated at the optimum temperature of about 35°C. The resulting vinegar contains about 9–10 per cent of acetic acid, but if pure diluted alcohol is used as the starting material, concentrations of the order of 12–14 per cent may be produced. These percentages represent a practical maximum, since at these concentrations the activity of the bacteria diminishes.

Vinegar may be described as the weak solution of acetic acid produced by the souring of wines and other fermented fruit and grain juices in the presence of air. Malt vinegar is prepared by a process similar to that involved in the manufacture of beer, except that the hops are omitted. The fermentation of barley produces a beer which is then soured by the quick-vinegar process to produce malt-vinegar.

Production of Glacial Acetic Acid. Anhydrous (or glacial) acetic acid is produced from the concentrated aqueous solution either by distillation from concentrated sulphuric acid or by efficient fractional distillation.

Properties of Acetic Acid. Glacial acetic acid is a colourless crystalline solid, m.p. 16·7°C and b.p. 118°C. It has a sharp "vinegar" taste and smell, and is soluble in water, alcohol and ether. It is used commercially as a solvent, as an intermediate in the manufacture of other organic substances, and most importantly in the manufacture of cellulose acetate rayon. Cellulose acetate is produced by the action of a mixture of equal weights of acetic acid and acetic anhydride containing about 1 per cent of sulphuric acid on cotton linters.

$$\{C_6H_{10}O_5\}_n \rightarrow \underset{\text{cellulose tri-acetate}}{\{C_6H_7O_2(OOC \,.\, CH_3)_3\}_n}$$

The resulting tri-acetate is partially hydrolyzed to the corresponding di-acetate which is collected, dried and later dissolved in acetone to produce the spinning solution.

Smaller quantities of acetic acid are also used in the manufacture of white lead (basic lead carbonate for paints, etc. (*see* p. 623)).

The chemical reactions of acetic acid are those already described in connexion with the general reactions of the fatty acid series. The following important points of difference from formic acid should, however, be noted.

1. Formic acid is a powerful reducing agent (acetic acid is not a reducing agent). Thus formic acid (and formates) reduce ammoniacal silver nitrate, Fehling's solution, mercuric chloride solution, and warm potassium permanganate.

2. Formic acid is an unexpectedly strong acid (acetic acid is only a very weak acid). Both, however, form metallic salts.

3. Concentrated sulphuric acid has no action on acetic acid, but when warmed with formic acid, a molecule of water is removed and carbon monoxide is liberated—

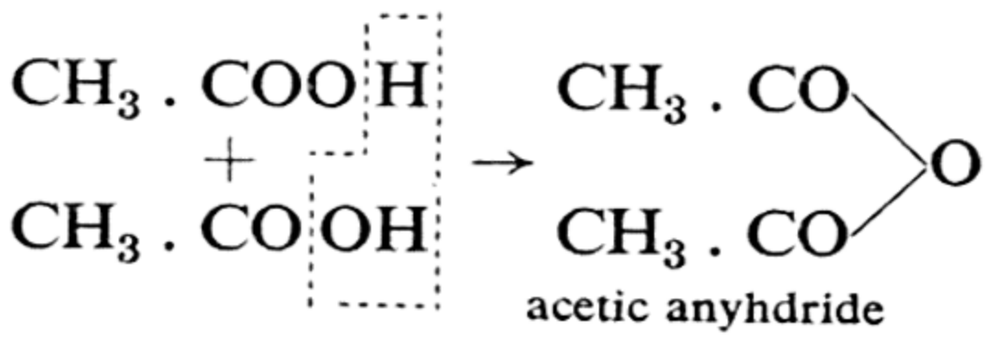
$$H . COOH \rightarrow CO + H_2O$$

4. With phosphorus pentachloride, acetic acid (anhydrous) is converted into acetyl chloride, $CH_3 . COCl$; formic acid, however, does not give a formyl chloride but only a mixture of carbon monoxide and HCl—

$$H . COOH \rightarrow [H . COCl] \rightarrow CO + HCl$$

$$CH_3 . COOH \rightarrow CH_3 . COCl$$

5. Glacial acetic acid is easily converted into acetic anhydride, for example on heating with phosphorus pentoxide; formic acid does not form an anhydride—



acetic anyhdride

6. Calcium formate when heated forms formaldehyde, H . CHO; calcium acetate, however, forms acetone, $CH_3 . CO . CH_3$.

7. Formic acid does not form substitution compounds with the halogens; acetic acid does—

$$CH_3 . COOH \rightarrow CH_2Cl . COOH \rightarrow CHCl_2 . COOH \rightarrow CCl_3 . COOH$$

8. Sodium formate forms sodium oxalate and hydrogen when heated.

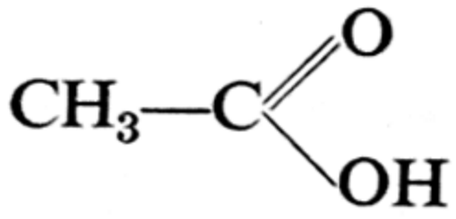
9. Sodium acetate heated with soda-lime liberates methane; sodium formate however liberates hydrogen and no hydrocarbon.

Structure of Acetic Acid. The molecular formula may be shown, by the usual methods, to be $C_2H_4O_2$.

Reaction with phosphorus pentachloride to liberate hydrogen chloride indicates the presence of an hydroxyl (—OH) group.

Reaction with chlorine in sunlight to form trichloracetic acid indicates that three of the hydrogen atoms are differently constituted in the molecule than the remaining hydrogen atom. That these three hydrogen atoms are attached to the same carbon atom, that is, are present as a methyl (—CH_3) group, is indicated by such reactions as the formation of ethane (CH_3 . CH_3) on electrolysis of acetic acid and the liberation of methane by the soda-lime reaction.

Since, therefore, acetic acid contains both an OH and a CH_3 radical, its formula must be



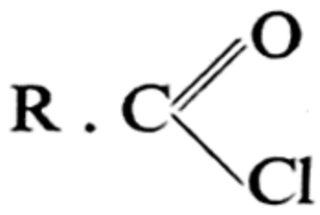
This formula is also in accord with all the other reactions of this acid.

ACID DERIVATIVES

In the discussion of the general reactions of the monobasic acids (*see* p. 925), compounds with names such as acyl chlorides, anhydrides, amides, esters and nitriles appeared. These compounds are known collectively as "acid derivatives," since they may be obtained from the acids by certain standard reactions. It is proposed to discuss each of these classes of compounds in the following sections.

Acyl Chlorides

These have the general formula



and are clearly derived from the acids by replacement of the hydroxyl (—OH) group by chlorine. The two most important members are acetyl chloride, CH_3 . COCl, derived from acetic acid, and benzoyl chloride, C_6H_5 . COCl, derived from the aromatic monobasic benzoic acid C_6H_5 . COOH. As a class, they are colourless liquids or solids, have a pungent odour, and are hydrolyzed by water. Acetyl chloride is immediately hydrolyzed by water and may, therefore, be prepared only under water free conditions.

Preparation of Acetyl Chloride. This is usually achieved by the action of phosphorus chlorides on glacial acetic acid. The preparation may conveniently be carried out by adding phosphorus tri-chloride slowly to glacial acetic acid in the apparatus as shown in the diagram. It may be necessary to cool the flask in the earlier stages of the reaction. The soda-lime tower serves to trap the liberated HCl gas. The temperature of the flask is then slowly raised to about 50°C until the evolution of HCl ceases.

The water-bath is then heated to 100°C and the acetyl chloride distilled over.

$$3CH_3 . C(=O)OH + 2PCl_3 \rightarrow 3CH_3 . C(=O)Cl + P_2O_3 + 3HCl$$

Thionyl chloride ($SOCl_2$) may be used in place of phosphorus trichloride in the above preparation.

Properties. The acyl chlorides, of which acetyl chloride is taken as a typical example, are characterized by a high order of reactivity, resembling in this respect, only more so, the alkyl halides.

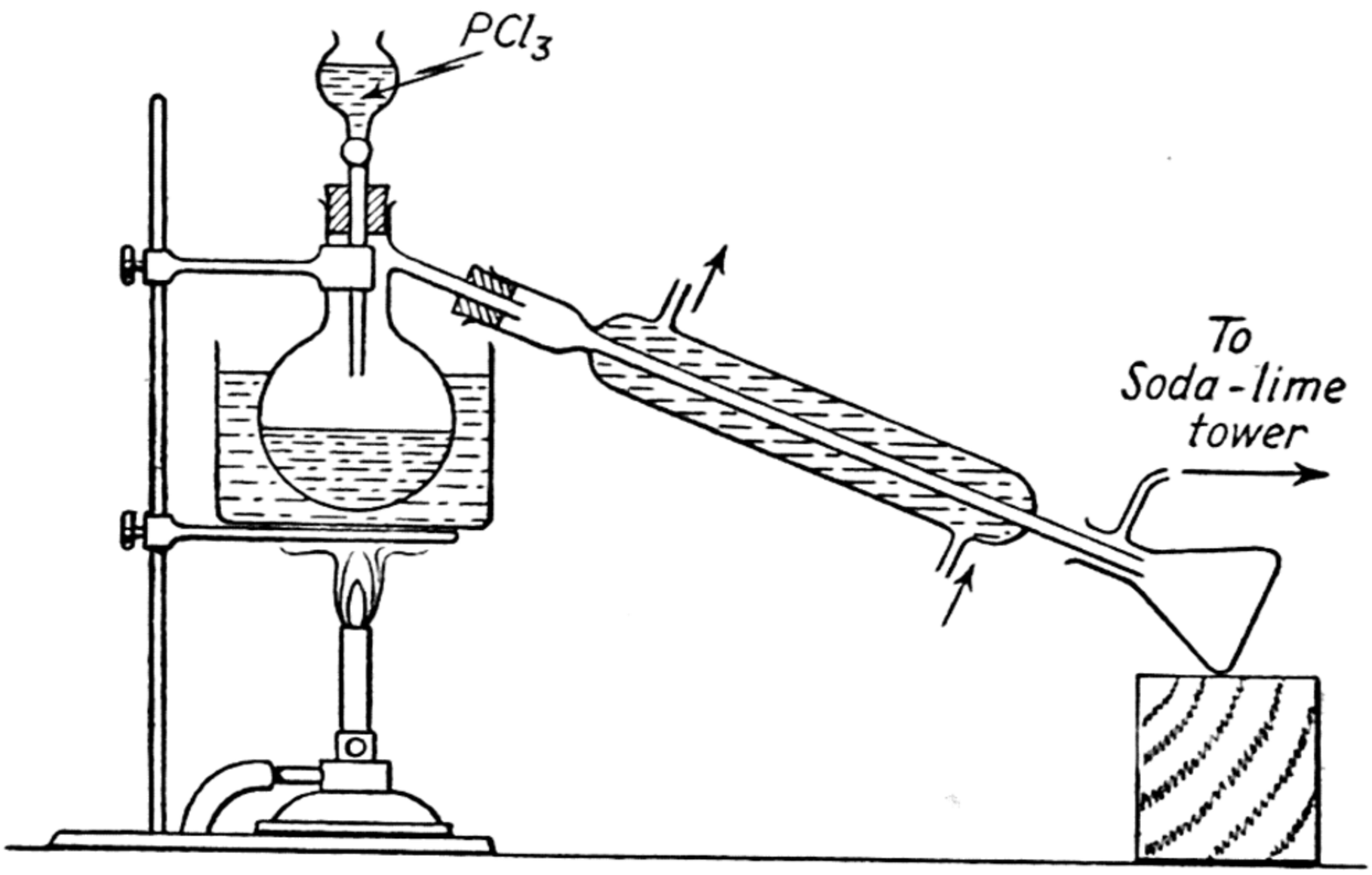


FIG. 267. Preparation of Acetyl Chloride

(*a*) Acetyl chloride fumes in air and reacts immediately even with cold water to reform acetic acid and liberate hydrogen chloride—

$$CH_3 . CO|Cl + H|OH \rightarrow CH_3 . COOH + HCl$$

(*b*) It reacts vigorously with alcohols to give the corresponding ester—

$$\underset{\text{acetyl chloride}}{CH_3 . CO|Cl} + H|OC_2H_5 \rightarrow \underset{\text{ethyl acetate}}{CH_3 . COOC_2H_5} + HCl$$

(*c*) It combines directly with ammonia to form acetamide, $CH_3 . CONH_2$, and with amines ($R . NH_2$) to form substituted amides—

$$CH_3 . COCl + H—NH_2 \rightarrow CH_3 . CONH_2 + HCl$$
$$CH_3 . COCl + H—NHR \rightarrow CH_3 . CONHR + HCl$$

(*d*) On warming with anhydrous sodium acetate, acetic anhydride is formed. If the sodium salt of, say, propionic acid is used, the corresponding mixed anhydride is formed—

$$CH_3 . COCl + NaOOC . C_2H_5 \rightarrow \begin{matrix} CH_3 . CO \\ \\ C_2H_5 . CO \end{matrix} \!\!> O + NaCl$$

$$CH_3 . COCl + NaOOC . CH_3 \rightarrow \begin{matrix} CH_3 . CO \\ \\ CH_3 . CO \end{matrix} \!\!> O + NaCl$$

acetic anhydride

(*e*) Acetyl chloride may be reduced by sodium amalgam or metallic sodium to acetaldehyde and finally ethyl alcohol—

$$CH_3 . COCl \rightarrow CH_3 . CHO \rightarrow CH_3 . CH_2 . OH$$

Acid Anhydrides

Acetic Anhydride, $(CH_3 . CO)_2O$, is a colourless liquid with a sharp pungent odour, resembling that of acetic acid. It boils at 137°C, is only slightly soluble in water and does not fume in air. It is a very much less vigorous reagent than acetyl chloride, which it resembles in its reactions towards alcohols, ammonia, amines, etc.

Preparation. Acetic anhydride is prepared by adding acetyl chloride to anhydrous sodium acetate—

$$CH_3 . CO\,Cl + Na\,OOC . CH_3 \rightarrow \begin{matrix} CH_3 . CO \\ \\ CH_3 . CO \end{matrix} \!\!> O + NaCl$$

The powdered anhydrous sodium acetate is placed in the flask which is cooled by immersion in cold water and the acetyl chloride added slowly from the dropping funnel. The mixture is periodically gently shaken. The apparatus is then assembled for distillation and the impure acetic anhydride very gently distilled over, using an air-condenser in place of the usual water-cooled condenser. The distillate is then purified by a further distillation, and the product, boiling between 135°–140°C, collected.

Acetic anhydride may also be prepared, although this is not the usual method, by the action of phosphorus pentoxide on glacial acetic acid.

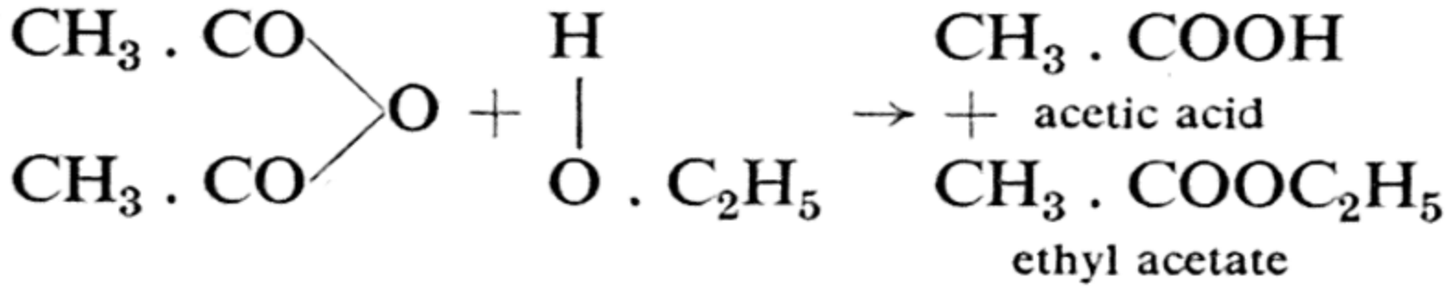
Some dibasic acids, such as succinic acid and phthalic acid, form cyclic anhydrides on heating alone—

$$\begin{matrix} CH_2 . COOH \\ | \\ CH_2 . COOH \end{matrix} \rightarrow \begin{matrix} CH_2 . CO \\ | \\ CH_2 . CO \end{matrix} \!\!> O + H_2O$$

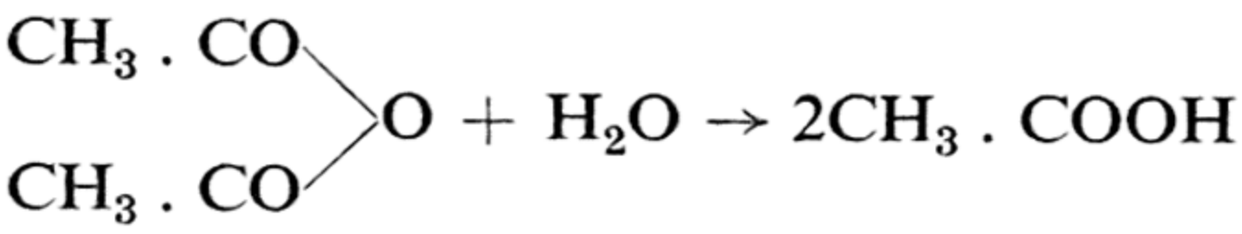
succinic acid

Properties. As a class, the acid anhydrides are neutral liquids or solids, with boiling points higher than those of the parent acids. They have an unpleasant pungent smell, are insoluble or very slightly soluble in water, but dissolve unchanged in most organic solvents. They resemble the acid chlorides in their chemical reactivity but are very much less reactive.

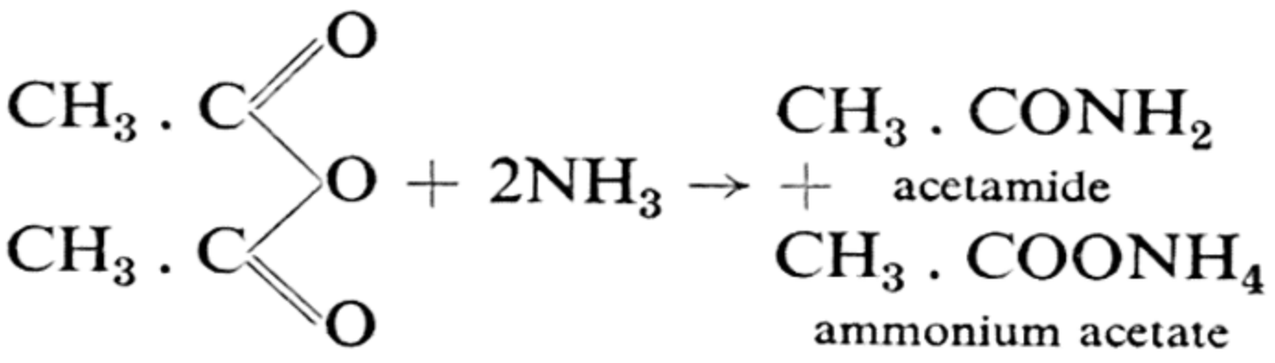
(*a*) With alcohols, reaction occurs on warming to form the ester and acid—



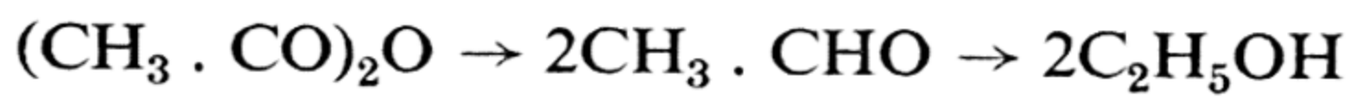
(*b*) Acetic anhydride hydrolyzes slowly on warming with water to form acetic acid—



(*c*) Acetic anhydride reacts with ammonia and with amines in the hot—

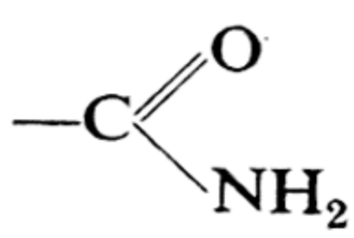


(*d*) Reduction with sodium amalgam or metallic sodium converts acetic anhydride successively to acetaldehyde and ethyl alcohol.

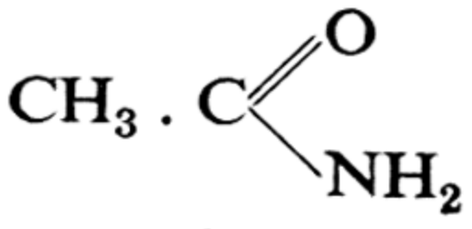


Amides

These compounds have the general formula R . $CONH_2$, and may be regarded as derived from the mono-basic acids by replacement of the OH group by the amino (—NH_2) group. They, therefore, have the characteristic amide group



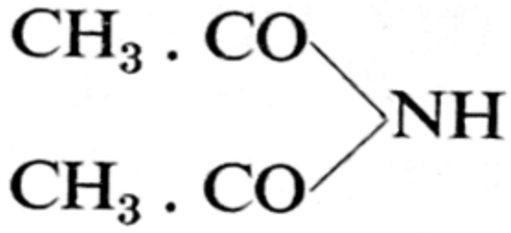
for example

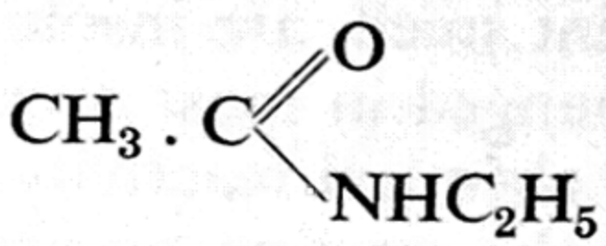


acetamide

Substituted amides are also known in which the hydrogen atoms of

this group are replaced by other acyl groups, alkyl groups or aryl groups,

e.g.  diacetamide

 ethyl acetamide etc.

Preparation. The general methods for preparing acid amides are—

1. Dehydration of the corresponding ammonium salt, for example, on heating the dry salt preferably in a sealed tube, (that is, under pressure)—

$$CH_3 . COONH_4 \rightarrow CH_3 . CONH_2 + H_2O$$

2. By the action of concentrated aqueous ammonia on acid chlorides, acid anhydrides or esters—

$$R . COCl + H—NH_2 \rightarrow R . CONH_2 + HCl$$
$$(R . CO)_2O + 2H—NH_2 \rightarrow R . CONH_2 + R . COONH_4$$
$$R . COOR' + H—NH_2 \rightarrow R . CONH_2 + R'OH$$

3. By hydrolysis of alkyl cyanides (nitriles) in presence of concentrated hydrochloric acid or strong sulphuric acid. The hydrolysis also occurs on boiling the cyanide with water—

$$R . C{\equiv}N + H_2O \rightarrow R . CONH_2$$

Acetamide, CH_3CONH_2, is best prepared by the first of these methods. Ammonium acetate is heated with excess of glacial acetic acid which helps to suppress the dissociation of the ammonium acetate into acetic acid and ammonia.

$$CH_3 . COONH_4 \rightarrow CH_3 . CONH_2 + H_2O$$

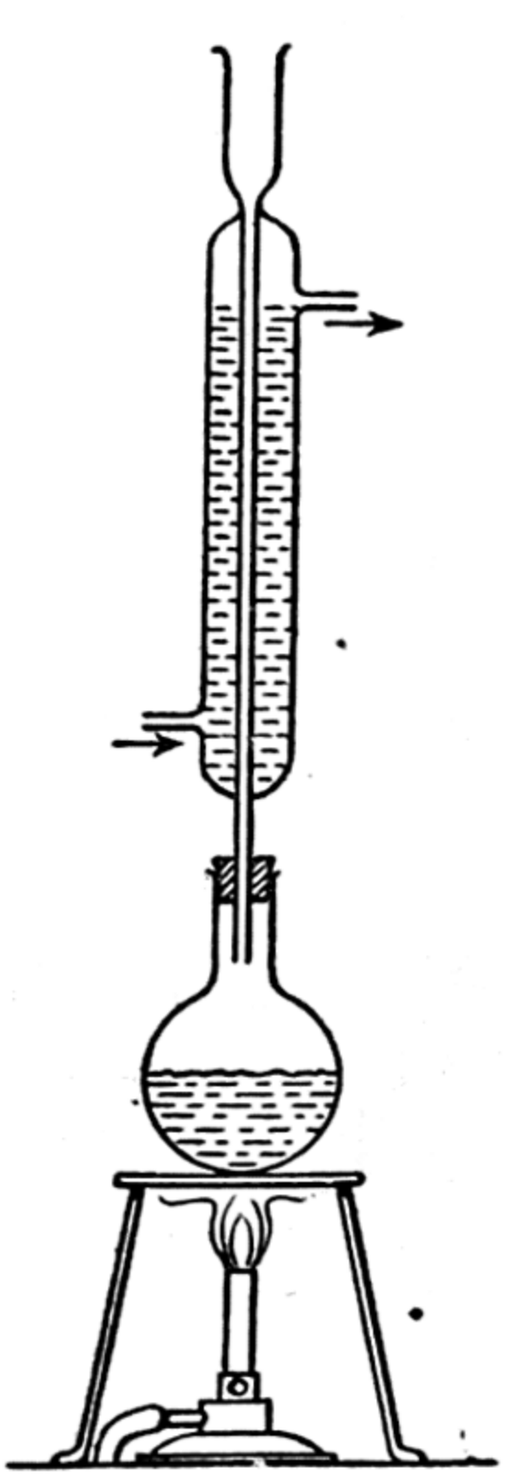


FIG. 268. Water-cooled Reflux Condenser

The ammonium acetate is prepared in situ by gradually adding powdered ammonium carbonate to glacial acetic acid. The resulting solution of ammonium acetate in acetic acid is then gently boiled for about 30 min. with an air-cooled reflux condenser. During this refluxing, the ammonium acetate is converted to acetamide. After removing the reflux condenser and fitting a side air-cooled condenser, the liquid is then distilled very slowly to allow the excess acetic acid and water to distil over first. The fraction boiling above 180°C is then collected and is mainly acetamide. A purer specimen may be obtained by redistilling and collecting the fraction boiling between 215°–225°C.

Properties. Acetamide is a colourless crystalline solid, m.p. 82°C and b.p. 222°C. It is readily soluble in water and in alcohol, and has a characteristic odour of mice due to the presence of small quantities of methyl acetamide, $CH_3CONHCH_3$, as impurity. It may be recrystallized from acetone in the form of long needles, and is then free from odour.

Apart from formamide, $H . CONH_2$, the amides are all solids with boiling points considerably higher than those of the corresponding acids, and show decreasing solubility in water with increase in molecular weight. Formamide, the first member of the series, is prepared by methods similar to those for acetamide, for example, by heating ammonium formate. It is a colourless liquid.

The general reactions of the amides are typified by those of acetamide.

(*a*) When heated with alkalis or on boiling with water, the amides are hydrolyzed to the acid and ammonia—

$$CH_3 . CONH_2 + H_2O \rightarrow CH_3 . COOH + NH_3 \rightarrow CH_3 . COONH_4$$

(*b*) The acids are also formed when the amides react with nitrous acid—

$$CH_3 . CO\boxed{N}\boxed{H_2 + O}\boxed{N}OH \rightarrow CH_3 . COOH + N_2 + H_2O$$

This latter reaction is similar to the formation of alcohols when primary amines are treated with nitrous acid (*see* p. 954)—

$$R . \boxed{N}\boxed{H_2 + O}\boxed{N}OH \rightarrow R . OH + N_2 + H_2O$$

(*c*) When heated with dehydrating agents, such as phosphorus pentoxide, amides are converted into the corresponding nitriles—

$$CH_3 . CONH_2 - H_2O \rightarrow CH_3 . CN$$

aceto-nitrile or methyl cyanide

(*d*) Amides may be converted into amines (by the Hofmann reaction) by treatment with bromine followed by the addition of sodium hydroxide solution. The reaction probably proceeds through the following stages—

(i) $CH_3 . CONH_2 + Br_2 \rightarrow HBr + CH_3 . CONHBr$

mono-bromo-acetamide

(ii) $CH_3 . CONHBr + NaOH \rightarrow H_2O + CH_3 . CON\begin{matrix}Na\\Br\end{matrix}$

sodium bromoacetamide

(iii) $CH_3 . CON\begin{matrix}Na\\Br\end{matrix} + H_2O \rightarrow NaBr + CO_2 + CH_3 . NH_2$

methylamine

(*e*) In general, amides are very weakly amphoteric in character. Thus, salts such as $CH_3 . CONH_2 . HCl$ are known but are very unstable and decompose on treatment with water. The weakly acidic character, on the other hand, is revealed by the replacement of one of the amide hydrogen atoms by a metal as in the above Hofmann reaction, and the formation of mercury salts by boiling the amide with mercuric oxide—

$$2CH_3 . CONH_2 + HgO \rightarrow (CH_3 . CONH)_2Hg + H_2O$$

Esters

Esters are formed by reaction between alcohols and acids, e.g.

$$CH_3 . CO\boxed{OH + H}OC_2H_5 \rightarrow \underset{\text{ethyl acetate}}{CH_3 . COOC_2H_5} + H_2O$$

The similarity between this reaction in which an acid reacts with an alcohol, and the reaction in which a salt is formed by the neutralization of an acid by a base, i.e.—

$$\text{Alcohol} + \text{Acid} \rightarrow \text{Ester} + \text{Water}$$
$$\text{Base} + \text{Acid} \rightarrow \text{Salt} + \text{Water}$$

suggests that esters are the organic counterpart of the inorganic salt. Esters, however, are not salts. They are purely covalent compounds and are typically organic in character. Thus, they are usually volatile liquids or solids (i.e. low melting points and boiling points), they are insoluble in ionizing solvents (water, etc.) but are soluble in non-ionizing solvents (that is, most organic solvents), and when they react with water, instead of forming an acid and a base, they form an acid and an *alcohol*. Since the latter reaction differs from the corresponding reaction of a salt, it is usually referred to as saponification—

Hydrolysis $Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3$

Saponification $CH_3 . COOC_2H_5 + H_2O \rightarrow CH_3 . COOH + C_2H_5OH$

The term saponification was originally applied to the production of the sodium salts of the acid when the esters present in natural fats were boiled with sodium hydroxide in the manufacture of soap (*see* pp. 431, 946), but the term is now applied generally to the hydrolysis of esters.

Two types of ester are known. The first, in which the ester is derived from an organic acid, for example ethyl acetate, and the second in which the ester is formed from an inorganic acid, for example, methyl chloride and ethyl sulphate. The alkyl halides have already been discussed and other important members of the second class will be discussed later. The first class, however, is clearly the larger and will be discussed first.

General Methods of Preparation. The reaction—

$$\text{Acid} + \text{Alcohol} \rightleftharpoons \text{Ester} + \text{Water}$$

is reversible and like most organic reactions occurs relatively slowly. It is, therefore, carried out by heating the acid and alcohol together in the presence of a suitable dehydrating agent. The latter appears both to remove the molecule of water formed (and so diminish the back-reaction) and also to catalyze the reaction.

(*a*) The procedure adopted when concentrated sulphuric is used as the dehydrating agent is explained in the following preparation of ethyl acetate. A mixture of equal volumes of ethyl alcohol and concentrated sulphuric acid is prepared by adding the acid cautiously to the alcohol with shaking. The mixture is then heated on an oil-bath to about 150°C and a mixture of equal volumes of ethyl alcohol and glacial acetic acid then added slowly from a tap-funnel at approximately the same rate at which the ethyl acetate distils over into the receiver. In the first stage, the sulphuric acid converts the alcohol into ethyl hydrogen sulphate and water, the latter being removed by the excess sulphuric acid—

$$C_2H_5OH + HHSO_4 \rightarrow C_2H_5HSO_4 + H_2O$$

The ethyl hydrogen sulphate then reacts with the acetic acid added during the second stage to form ethyl acetate and liberate the sulphuric acid, which forms fresh ethyl hydrogen sulphate with the alcohol added simultaneously with the acetic acid—

$$C_2H_5HSO_4 + CH_3 . COOH \rightarrow CH_3 . COOC_2H_5 + H_2SO_4$$

When all the acetic acid-alcohol mixture has been added, the distillate is first shaken with a strong solution of sodium carbonate (in a separating funnel) to neutralize and remove any free acetic and sulphurous acid, and the upper ethyl acetate layer then separated. This is then shaken with a concentrated solution of calcium chloride to remove any free ethyl alcohol, and the ethyl acetate layer again separated. It is then dried by adding some anhydrous calcium chloride, and if necessary redistilled, the fraction boiling between 74°–79°C being collected (boiling point of ethyl acetate is 77°C).

(*b*) In the *Fischer-Speier* method the catalyst and dehydrating agent is anhydrous hydrogen chloride. Ethyl alcohol is first saturated with dry hydrogen chloride and then mixed with an equal volume of glacial acetic acid. The ester is then formed by heating the mixture under reflux for about half an hour. The liquid is then cooled and the ethyl acetate separated by the method adopted above.

Esters may also be prepared in almost quantitative yield by treating the alkyl halide with the silver salt of the acid, e.g.

$$CH_3 . COOAg + I{-}C_2H_5 \rightarrow CH_3 . COOC_2H_5 + AgI \downarrow$$

The reaction of alcohols with acid chlorides and with acid anhydrides to form esters have already been described in connexion with the properties of these two classes of compounds—

$$CH_3 . COCl + HOC_2H_5 \rightarrow CH_3 . COOC_2H_5 + HCl$$

$$(CH_3 . CO)_2O + C_2H_5OH \rightarrow CH_3 . COOC_2H_5 + CH_3 . COOH$$

Properties. The esters are mostly colourless liquids or solids, sparingly soluble in water but very soluble in organic solvents, and have usually very pleasant fruity odours. Some examples of the latter are given in the following table.

TABLE 118

Some Common Esters

Ester	B.P. (°C)	Odour
Ethyl formate	55	"Rum" flavour
Ethyl acetate	77	Apple
Iso-amyl acetate	138	"Pear-drop" essence
Ethyl butyrate	120	"Pine-apple" essence
Ethyl isovalerate	134	"Apple" essence
Iso-amyl acetate	139	"Banana" essence
Methyl salicylate	224	Oil of Wintergreen

They are, therefore, used as artificial essences and perfumes. Ethyl acetate and amyl acetate are particularly important as industrial solvents, for example, in the manufacture of cellulose lacquers. Others, such as dibutyl phthalate, are used as "plasticizers" in the manufacture of certain plastics.

The more important of the reactions of the esters are—

(*a*) Saponification on treatment with water, acids or alkalis. The hydrolysis occurs only slowly with water even at the boiling point but occurs more readily with the stronger acids, such as hydrochloric and sulphuric acids—

$$CH_3 . COOC_2H_5 + H_2O \rightarrow CH_3 . COOH + C_2H_5OH$$

This reaction offers a simple experiment for the measurement of reaction velocity in physical chemistry. The results show that the rate of saponification or hydrolysis is proportional to the hydrogen-ion concentration (H^+); the stronger the acid the more effective it is as a catalyst. The hydrolysis occurs most rapidly, however, with the alkalis, and particularly so with alcoholic solutions of the latter.

$$CH_3 . COOC_2H_5 + NaOH \rightarrow CH_3 . COONa + C_2H_5OH$$

(*b*) Esters react with ammonia (or amines) to form amides (or substituted amides) and the alcohol—

$$CH_3 . CO|OC_2H_5 + H|-NHR \rightarrow CH_3 . CONHR + C_2H_5OH$$

(*c*) When heated with hydrogen iodide, the alkyl iodide and free acid are formed—

$$CH_3 . COO|C_2H_5 + I|H \rightarrow CH_3 . COOH + C_2H_5I$$

(*d*) With phosphorus pentachloride, reaction occurs to form the acyl chloride and alkyl chloride—

$$CH_3 . COOC_2H_5 + PCl_5 \rightarrow CH_3 . COCl + C_2H_5Cl + POCl_3$$

Naturally Occurring Esters

These comprise the oils, fats and waxes of the animal, vegetable and fish kingdoms, and include the well-known butter fat, lard, palm-oil, coconut oil, cod liver oil, whale oil, beeswax, carauba wax, and *spermaceti*. They are all esters of the higher monobasic acids (palmitic, stearic, oleic, etc.), but oils and fats differ chemically from waxes in being esters of the trihydric alcohol, glycerol, whereas waxes are the esters of higher monohydric alcohols, such as, cetyl alcohol, $C_{16}H_{33}OH$ (in *spermaceti*) and myricyl alcohol, $C_{30}H_{61}OH$ (in beeswax)—

Oils and Fats—

Esters of the trihydric glycerol, known as *glycerides*

e.g.

$$\begin{array}{l} CH_2OOC . R \\ | \\ CHOOC . R \\ | \\ CH_2OOC . R \end{array}$$

Waxes—

Esters of higher monohydric alcohols, e.g. R′ . COOR

Dealing first with the oils and fats, these are complex natural mixtures of the glycerides of various higher aliphatic acids which contain an even number of carbon atoms. The main difference between an oil and a fat is that the latter has a higher melting point and so is solid at ordinary temperatures. The lower melting point of oils are due to the presence of glycerides of certain unsaturated fatty acids, such as oleic acid ($C_{17}H_{33} . COOH$) and linoleic acid ($C_{17}H_{31} . COOH$) which melt at lower temperatures than the glycerides of the corresponding saturated acids.

This is shown, for example, in the following figures for the melting points of the glycerides of palmitic and stearic acids (both saturated), and of oleic acid (unsaturated).

Palmitin	$C_3H_5(OOC \cdot C_{15}H_{31})_3$ m.p. 63°C
Stearin	$C_3H_5(OOC \cdot C_{17}H_{35})_3$ m.p. 65·5°C
Olein	$C_3H_5(OOC \cdot C_{17}H_{33})_3$ m.p. — 6°C

It follows that if the unsaturated acids present in oils could be converted into saturated acids, the melting points of the glycerides would be increased and the oils converted into fats. This is the principle involved in the modern industrial process for converting oils into fats by hydrogenation (*see* below).

In the Table on p. 945 are listed the acids which occur as glycerides in the various oils and fats. In subsequent Tables, the composition of particular oils and fats are given with reference to the principal acids present (as glycerides).

Butter Fat differs from all the other fats in containing glycerides of butyric acid and other lower acids, such as caproic, caprylic and capric acids. The peculiar odour of rancid butter is due to the formation of free butyric acid, whilst the characteristic flavour of fresh butter is due to the presence of a trace of diacetyl, a di-ketone.

Margarine is a butter substitute, consisting of an emulsified blend of various fats (other than butter) with approximately the same melting point as butter. The particular blend may vary with the local climatic conditions (e.g. winter or summer), and with fluctuations in the price of the various fats, but the following blend may be taken as representative.

	per cent
Palm kernel oil	50
Coconut oil	15
Beef fat ("premier jus") . . .	15
Ground-nut oil	10
Cotton-seed oil	10

The hard beef fat may be replaced by solid vegetable fats, such as coconut or palm oil, or by hydrogenated oils (cotton-seed, whale, and ground-nut oils, etc.). The mixture of fats is churned with milk to emulsify them and to impart a "butter" flavour, and then rolled and pressed until it emerges as a water-in-fat emulsion with about the same water content (13–16 per cent) as butter. A definite proportion of vitamin A and D concentrates is then added together with the required colouring matter.

Cooking Fats. The supply of suitable substitutes for lard has been considerably increased in recent years by hydrogenating cotton-seed oil, ground-nut oil, soya-bean oil, etc. The present world shortage of edible

Table 119

Higher Saturated and Unsaturated Acids Present in Glycerides

Saturated Acids		Unsaturated Acids		
		Name	No. of Double Bonds	Formula
Butyric acid	$C_3H_7 . COOH$			
Caproic acid	$C_5H_{11} . COOH$			
Caprylic acid	$C_7H_{15} . COOH$			
Capric acid	$C_9H_{19} . COOH$			
Lauric acid	$C_{11}H_{23} . COOH$	Lauroleic acid	1	$C_{11}H_{21} . COOH$
Myristic acid	$C_{13}H_{27} . COOH$	Myristoleic acid	1	$C_{13}H_{25} . COOH$
Palmitic acid	$C_{15}H_{31} . COOH$	Palmitoleic acid	1	$C_{15}H_{29} . COOH$
Stearic acid	$C_{17}H_{35} . COOH$	Oleic acid	1	$C_{17}H_{33} . COOH$
Arachidic acid	$C_{19}H_{39} . COOH$	Linoleic acid	2	$C_{17}H_{31} . COOH$
		Linolenic acid	3	$C_{17}H_{29} . COOH$

Oil or fat	*Mainly composed of glycerides of—*
	Vegetable Oils and Fats
Olive oil . . .	Oleic acid (85); palmitic acid (7); linoleic acid (6).
Ground-nut oil . .	Oleic acid (60); linoleic acid (21); palmitic acid (7); stearic acid (5).
Coconut oil (a fat) .	Lauric acid (51); myristic acid (18·5); caprylic acid (9·5); palmitic acid (7·5).
Palm-kernel oil (a fat) .	Lauric acid (52); oleic acid (16); myristic acid (15).
Palm oil (a fat) . .	Oleic acid (48·5); palmitic acid (35·5).
Cotton-seed oil . .	Linoleic acid (53·6); oleic acid (23).
Linseed oil . . .	Linoleic acid (62); linolenic acid $C_{17}H_{29}COOH$ (24).
	Animal Fats
Butter . . .	Oleic acid (40); palmitic acid (29); stearic acid (7·6); myristic acid (3·1); butyric acid (3·1).
Lard	Oleic acid (40·3); palmitic acid (28·5); stearic acid (21·4).
Beef tallow . .	Oleic acid (48); palmitic acid (30); stearic acid (18) (approx.).
Mutton tallow . .	Oleic acid (45); stearic acid (27); palmitic acid (23) (approx.).
	Fish Oils
Whale oil . . .	Oleic acid (35); palmitoleic acid (18); palmitic acid (10); linoleic acid (9); and higher acids.
Sperm oil . . .	Oleic acid (35); palmitoleic acid (24); and higher acids.
Cod liver oil . .	Oleic acid (25); palmitoleic acid (20); palmitic acid (8·5) and acids of higher molecular weight including many with several double bonds.

Note: Figures given in brackets are percentages.

fats is reflected in the British Governments' efforts to increase the production of ground nuts in Africa. These nuts, when compressed ("expressed") produce ground-nut oil (40–50 per cent), and leave an oil-cake which contains valuable protein matter and about 10 per cent of residual oil which makes it very valuable as a cattle food.

Hydrogenation of Oils. It has been seen that oils differ from fats only in their lower melting points due to the presence of glycerides of unsaturated acids. Since fats are more useful industrially, and are much preferred by the housewife to oils, considerable quantities of oils are nowadays "hardened" by hydrogenation in the presence of a catalyst. During this process, the unsaturated acids are converted to saturated acids. There are various modifications of the process, but they all involve heating the oil with hydrogen under 2–5 atmospheres pressure at about 200°C in the presence of nickel as catalyst. The process is in fact a modification of the Sabatier-Senderens reaction described earlier in connexion with hydrogenating unsaturated hydrocarbons. When the oil has hardened sufficiently (as indicated by cooling test samples), the process is stopped and the hot liquid fat filtered off from the nickel catalyst. Very small quantities of nickel, however, always remain in the resulting fat.

Waxes. These may be divided into two chemically different classes—

(*a*) Mineral waxes, such as the various grades of paraffin wax. These are not esters, but simply mixtures of various higher hydrocarbons.

(*b*) Animal and vegetable waxes which are esters of various higher mono-hydric alcohols (which distinguishes them from edible oils and fats). Examples include animal waxes such as beeswax (esters of myricyl alcohol), wool wax, spermaceti (esters of cetyl alcohol—obtained from whale sperm oil) and vegetable waxes such as carnauba, candellilo, esparto and shellac waxes.

Soaps

When fats and oils, such as tallow, palm-oil, coconut oil, etc., are boiled with sodium hydroxide, they are hydrolyzed ("saponified") to produce the sodium salt of the fatty acids and liberate glycerol

$$\begin{array}{l} CH_2O \\ | \\ CH\,.\,O \\ | \\ CH_2O \end{array}\begin{array}{l} OC\,.\,C_{17}H_{35} \\ OC\,.\,C_{17}H_{35} \\ OC\,.\,C_{17}H_{35} \end{array} + \begin{array}{l} NaOH \\ NaOH \\ NaOH \end{array} \rightarrow \begin{array}{l} CH_2OH \\ | \\ CH\,.\,OH \\ | \\ CH_2OH \end{array} + 3C_{17}H_{35}\,.\,COONa$$

stearin or tri-stearin — glycerol — sodium stearate

The resulting sodium salts of the higher fatty acids are known as soaps. At the end of the boiling operation, common salt is added, either as the solid or in solution, to salt-out the soap. The latter separates from the solution

and rises to the surface as a granular curdy mass. The lower brine solution containing the glycerine is then drawn off from the bottom, and the granular soap which remains behind in the soap pan is then made homogeneous and pasty by mixing with hot water or by blowing in steam. It is then run off into suitable wooden moulds and allowed to solidify, or it may be quickly cooled by allowing it to fall on to an internally-cooled rotating drum. The resulting thin sheets of soap are then broken into smaller pieces and rapidly dried in a current of hot air.

In the manufacture of toilet soap, perfume and colouring matter are added at this stage, and the mixture again made homogenous by milling before passing to the final compressor and stamping machine. In the manufacture of soap flakes, however, the soap is milled between water-cooled steel rollers to produce flakes about 0·005 in. thick. Soap powders are produced by adding various sodium salts, such as the carbonate, silicate and phosphate, to the liquid soap in the soap pan, and then spraying the resulting mixture into a rapid stream of hot air. The droplets are in this way rapidly dried to form hollow globular particles, which are sold as soap powders.

Hard soaps are formed when sodium hydroxide is used, and soft soaps when potassium hydroxide is used. The latter are prepared by boiling oils, such as whale oil, linseed oil, or cotton-seed oil with potassium hydroxide, and omitting the salting-out operation. These soft soaps therefore retain the glycerol liberated during the saponification.

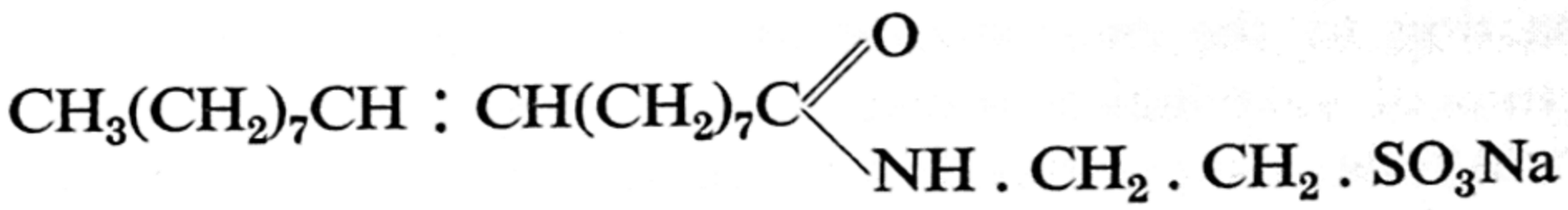
Instead of boiling fats with sodium or potassium hydroxide solution, the fats may be hydrolyzed into glycerol and the free acids, and the latter then converted into soaps or used for other purposes.

$$\underbrace{\begin{array}{l}CH_2O\\ |\\ CH{-}O\\ |\\ CH_2O\end{array}\begin{array}{l}OC\,.\,C_{15}H_{31}\\ OC\,.\,C_{15}H_{31}\\ OC\,.\,C_{15}H_{31}\end{array}}_{\text{palmitin}}\begin{array}{l}HO{-}\\ HO{-}\\ HO{-}\end{array}\begin{array}{l}{-}H\\ {-}H\\ {-}H\end{array} \rightarrow \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{glycerol}\end{array} + 3C_{15}H_{31}\,.\,COOH \quad \text{palmitic acid}$$

One such method consists in steam distilling a mixture of the fat with concentrated sulphuric acid; a second process heats the fat in an autoclave under pressure with water (together with small amounts of lime, magnesia or zinc oxide); yet a third, and more modern process, is to treat the fat with about 1 per cent of Twitchell reagent and water at 100°C. Twitchell reagent is naphthalene sulphonic acid, prepared by the action of concentrated sulphuric acid on naphthalene, and possesses the remarkable property of catalyzing the saponification of esters.

Modern Detergents other than Soaps. The above brief account of soap would not be complete without some mention of the present day trend to

replace soaps by other materials the manufacture of which do not involve the consumption of valuable edible oils and fats. These are mostly produced by sulphonating mineral oils, non-edible oils such as castor oil, rape-oil, etc., higher alcohols, such as lauryl and stearyl alcohols. These compounds or their salts (e.g. sodium salts) are best described as surface-active agents, and are used extensively as detergents (i.e. cleaning agents), emulsifiers, and wetting agents. Examples include Teepol, Turkey-red oil (sulphonated castor oil), Dreft (mainly sodium lauryl sulphate), Drene (triethanolamine lauryl sulphate) and Igopon T which is a sodium salt of a complex fatty acid amide with the formula



The latter is stable in both acid and alkaline solutions and does not give a precipitate with calcium and magnesium salts.

Esters of Inorganic Acids

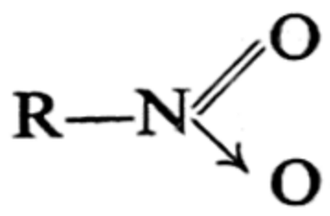
These are formed by the usual methods, for example, by the action of the acid on the alcohol in the presence of a dehydrating agent. The alkyl halides, discussed in an earlier chapter, are typical inorganic esters. Other examples include ethyl hydrogen sulphate, $C_2H_5 . HSO_4$, and di-ethyl sulphate, $(C_2H_5)_2SO_4$, and these two examples serve to remind us that when the acid is polybasic, acid esters are formed as well as the normal ester.

Di-methyl Sulphate is, perhaps, the most important of the sulphate esters, being used in considerable quantities for the purpose of introducing a methyl group into the molecule of another organic compound. It is a colourless oil, b.p. 188°C, is very poisonous and dangerous to handle, and is prepared by distilling methyl hydrogen sulphate under reduced pressure.

$$2CH_3 . HSO_4 \rightarrow (CH_3)_2SO_4 + H_2SO_4$$

Methyl Hydrogen Sulphate is prepared, like ethyl hydrogen sulphate, by the action of fuming sulphuric acid on methyl alcohol, or by heating the alcohol with concentrated sulphuric acid.

Nitrous Esters (and Nitro-compounds). Two classes of compounds are known with the general formula $R . NO_2$. The first of these are the esters of nitrous acid and have the structural formula, R—O—N=O. These are the nitrites. The nitro-compounds which form the second class have the formula



The main differences between these two isomeric series of compounds are summarized in the following table.

TABLE 120

Properties of Nitrites and Nitro-paraffins

Nitrites R—O—N=O	Nitro-paraffins R—N(=O)—O
Preparation. By the action of nitrites on alcohols in the presence of conc. H_2SO_4, the reaction being carried out in a freezing mixture	By distilling a mixture of silver nitrite with the appropriate alkyl iodide— $C_2H_5I + AgNO_2 \rightarrow AgI + C_2H_5.NO_2$
Easily saponified, for example by aqueous KOH— $C_2H_5O—N=O + KOH \rightarrow C_2H_5OH + KNO_2$	Form a salt with alkalis, and are not saponified— $C_2H_5NO_2 + KOH \rightarrow C_2H_4KNO_2 + H_2O$
With reducing agents, such as nascent hydrogen, the nitrites give the alcohol and hydroxylamine, (NH_2OH)— $C_2H_5ONO + 4\bar{H} \rightarrow C_2H_5OH + NH_2OH$	With reducing agents they form the very important amines, e.g. $R.NH_2$ $C_2H_5NO_2 + 6\bar{H} \rightarrow C_2H_5NH_2 + 2H_2O$
Nitrites are low boiling esters and have the N in the trivalent state.	Nitroparaffins are not esters, have relatively high boiling points and the N is pentavalent.

CHAPTER 33

AMINES

THE *amines* may be considered to be ammonia derivatives obtained by replacement of the hydrogen by alkyl (or aryl) groups. It follows that there should be three classes of amines, corresponding to the introduction of one, two or three such groups into the ammonia molecule, e.g.—

Primary amines, e.g. $CH_3 . NH_2$
methylamine

Secondary amines, e.g. $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\rangle NH$
dimethylamine

Tertiary amines, e.g. $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\rangle N{-}CH_3$
trimethylamine

Compounds of the type $[R_4N]X$, corresponding to ammonium salts, are also known. Although these may also be regarded as amines, since they are derived from ammonia, it is usual to refer to them as quaternary ammonium compounds, e.g. $[(CH_3)_4N]OH$, known as tetramethyl ammonium hydroxide. We shall defer the discussion of this last class until later in the present chapter, and deal first with the primary, secondary and tertiary amines.

Preparation. The amines were originally prepared directly from ammonia by heating the appropriate halide (e.g. C_2H_5I) with alcoholic ammonia in a sealed tube at about 100°C. The following reactions occurred to form a mixture of the above four types of amines—

$$NH_3 + C_2H_5I \rightarrow C_2H_5NH_2 + HI$$
$$C_2H_5NH_2 + C_2H_5I \rightarrow (C_2H_5)_2NH + HI$$
$$(C_2H_5)_2NH + C_2H_5I \rightarrow (C_2H_5)_3N + HI$$
$$(C_2H_5)_3N + C_2H_5I \rightarrow [(C_2H_5)_4N]I$$

These amines, present in the mixture as their HI salts, were then separated with difficulty by various methods, only one of which will be described here.

(*a*) Potassium hydroxide solution is added and the mixture then

distilled. The distillate contains $EtNH_2$, Et_2NH and Et_3N, and the non-volatile $[Et_4N]OH$ remains behind.

(*b*) The distillate is then treated with benzoyl chloride, C_6H_5COCl.

$$EtNH_2 \rightarrow Et \,.\, NH \,.\, OC \,.\, C_6H_5 \quad . \quad . \quad . \quad (i)$$

$$Et_2NH \rightarrow \begin{matrix} Et \\ \\ Et \end{matrix}\!\!\rangle N \,.\, CO \,.\, C_6H_5 \quad . \quad . \quad . \quad (ii)$$

$$Et_3N \text{ (does not react with } C_6H_5 \,.\, COCl) \quad . \quad . \quad (iii)$$

The separation of (i), (ii) and (iii) is then based on the facts that—

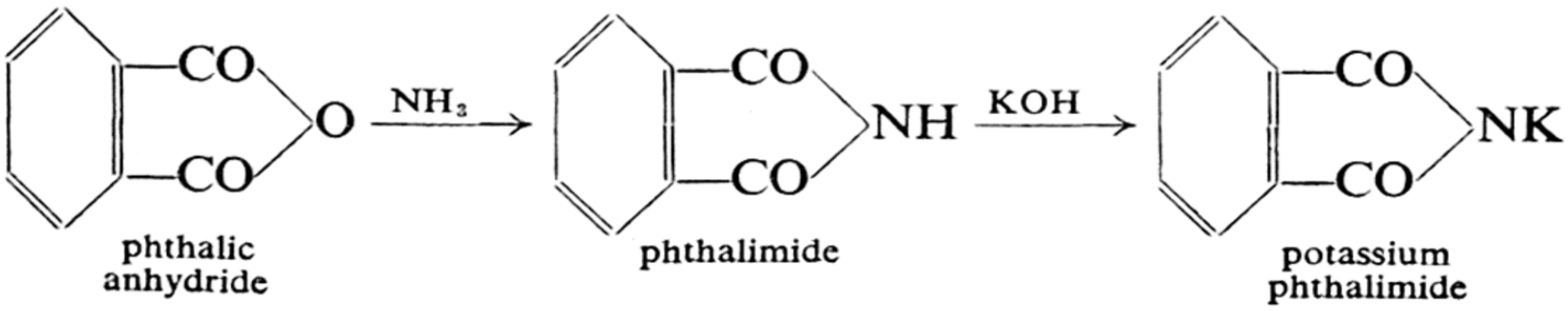
(i) is soluble in KOH ($\rightarrow Et.NK.CO.C_6H_5$); (ii) and (iii) are not; (ii) is non-volatile; (iii) is volatile.

The procedure, therefore, is to add potassium hydroxide solution, and extract with ether to remove (ii) and (iii). Distillation of this ether extract then separates (iii) from (ii). The primary and secondary amines are then recovered from (i) and (ii) by hydrolyzing with a strong acid.

Direct methods for preparing primary and secondary amines have replaced the above method, but tertiary and quaternary amines are prepared by this method.

Primary Amines. Three methods are available for the preparation of primary amines.

(*a*) *Gabriel's Synthesis.* The following stages are involved—



(*b*) *Hofmann's Reaction.* Conversion of an amide into a primary amine by reaction with bromine and potassium hydroxide.

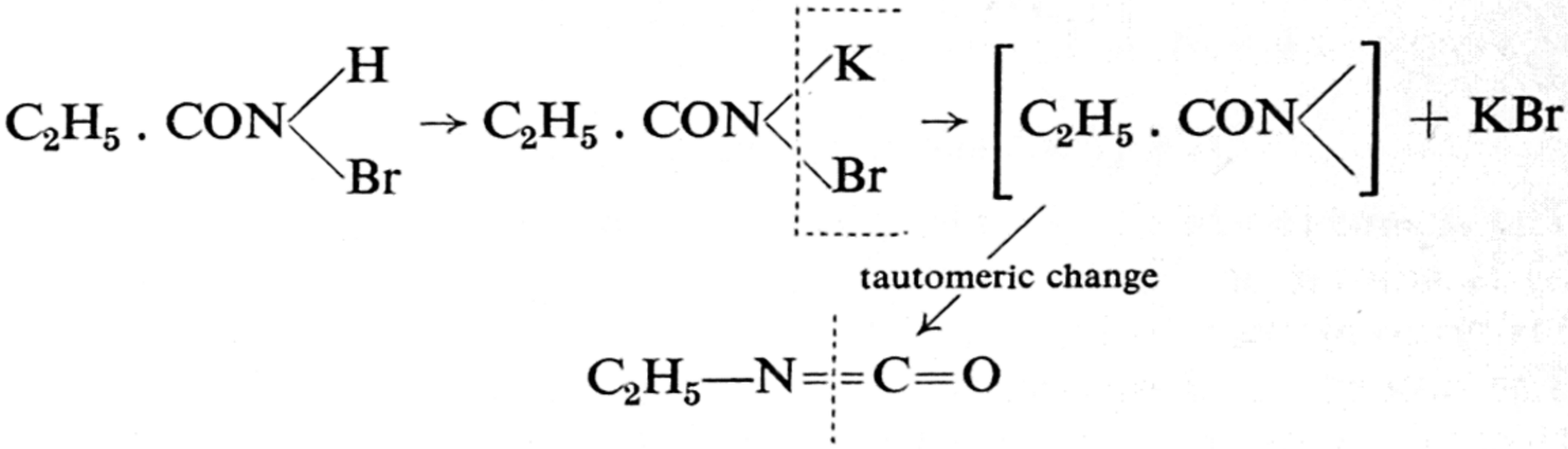
(i) The amide is cautiously mixed with bromine, and then KOH solution slowly added until the colour of the bromine disappears—

$$C_2H_5 \,.\, CONH_2 \,(+ Br_2 + KOH) \rightarrow C_2H_5 \,.\, CONHBr$$

(ii) The monobromo-amide is then slowly added to a concentrated aqueous solution of potassium hydroxide, and the ethylamine subsequently distilled over.

$$C_2H_5 . CONHBr + 3KOH \rightarrow C_2H_5 . NH_2 + KBr + K_2CO_3 + H_2O$$

The mechanism of the latter reaction appears to be—



which is hydrolyzed by the KOH to give $C_2H_5 . NH_2 + K_2CO_3$

(*c*) *By reduction*, for example via sodium and alcohol or tin and hydrochloric acid, of the corresponding nitriles and nitro-compounds—

$$CH_3 . CN (+ Na + \text{alcohol}) \rightarrow \underset{\text{ethylamine}}{CH_3 . CH_2 . NH_2}$$

$$CH_3 . NO_2 (+ Sn + HCl) \rightarrow \underset{\text{methylamine}}{CH_3 . NH_2}$$

Thus to convert methyl alcohol into ethylamine the following reactions are involved—

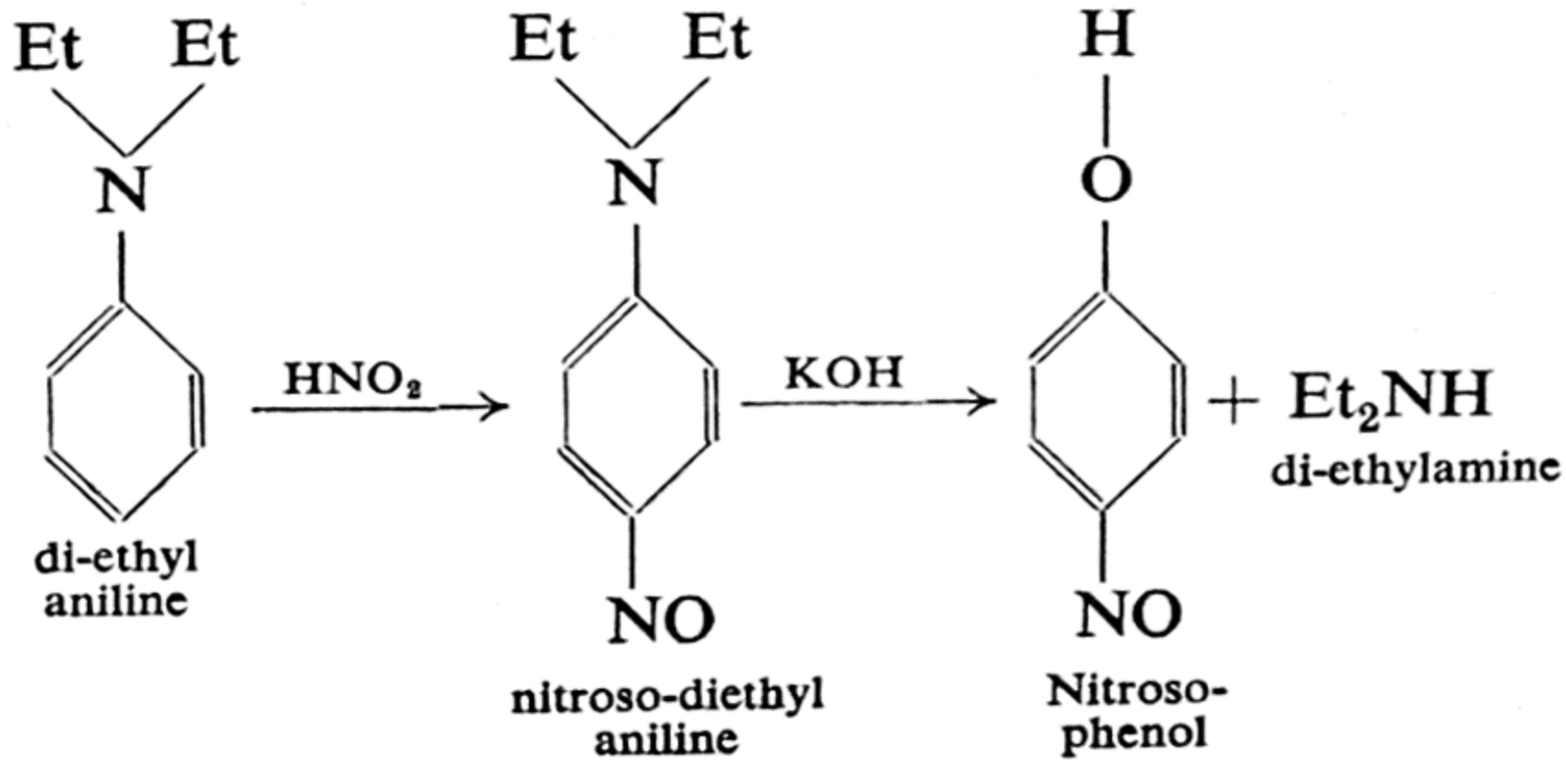
$$CH_3OH \xrightarrow{P \text{ and } I_2} CH_3I \xrightarrow{KCN} CH_3 . CN \xrightarrow{H} CH_3 . CH_2 . NH_2$$

and to convert methyl alcohol into methylamine—

$$CH_3OH \xrightarrow{P \text{ and } I_2} CH_3I \xrightarrow{AgNO_2} CH_3 . NO_2 \xrightarrow{H} CH_3 . NH_2$$

Secondary amines are usually prepared from aniline, $C_6H_5 . NH_2$, the reactions involved being—

$$C_6H_5 . NH_2 + C_2H_5I \text{ (excess)} \rightarrow C_6H_5 . N(Et)_2$$



Secondary (and tertiary amines) are also prepared from primary amines by reaction with a suitable alkylating agent, such as di-methyl sulphate—

$$CH_3 . NH_2 + (CH_3)_2SO_4 \rightarrow (CH_3)_2NH + CH_3 . HSO_4$$

$$(CH_3)_2NH + (CH_3)_2SO_4 \rightarrow (CH_3)_3N + CH_3 . HSO_4$$

Properties of Amines. The lowest members are gases, very soluble in water and have a fishy (ammoniacal) odour. In these properties they resemble ammonia. The lower members are also inflammable, differing in this respect from ammonia which only burns in an atmosphere of oxygen. The solubility, volatility and odour all decrease with increase in molecular weight.

The more important chemical reactions include—

(*a*) They resemble ammonia in their basic properties. Thus they form salts with acids, and these salts have the same ammonium type of formula—

$$\begin{cases} NH_3 + HCl \rightarrow \underset{\text{ammonium chloride}}{[NH_4]Cl} \\ CH_3NH_2 + HCl \rightarrow \underset{\text{methyl ammonium chloride}}{[CH_3NH_3]Cl} \end{cases}$$

$$\begin{cases} 2NH_3 + H_2SO_4 \rightarrow \underset{\text{ammonium sulphate}}{[NH_4]_2SO_4} \\ 2CH_3NH_2 + H_2SO_4 \rightarrow \underset{\text{methyl ammonium sulphate}}{[CH_3NH_3]_2SO_4} \end{cases}$$

(*b*) Like ammonia, the amines form double salts with the chlorides of certain metals, such as gold and platinum. Thus, the platini-chlorides may be prepared by dissolving the amine in hydrochloric acid and adding chloroplatinic acid, H_2PtCl_6—

$$2CH_3NH_2 + H_2PtCl_6 \rightarrow [CH_3NH_3]_2PtCl_6$$

These chloroplatinates are extremely insoluble and decompose quantitatively on heating to leave a residue of metallic platinum. They are therefore used in organic analysis to determine molecular weights of unknown amines. Thus, if we represent the amine by "B," the formula of the resulting chloroplatinate will be $[BH]_2 . PtCl_6$ (or $B_2H_2PtCl_6$)

$$\text{Then, } \frac{\text{Weight of chloroplatinate}}{\text{Weight of platinum residue}} = \frac{2B + H_2PtCl_6}{Pt} = \frac{2B + 410}{195}$$

The solution to this equation then gives "B," the molecular weight of the amine.

(*c*) The basic properties of the amines increase with increase in the number of alkyl groups. They all form hydroxides, the basicity increasing in the order: primary → secondary → tertiary → quaternary. The basicity of the quaternary ammonium hydroxide, however, is very much greater than the tertiary ammonium hydroxide, and approximates closely to that of sodium and potassium hydroxides. The replacement of the last of the hydrogen atoms in ammonium hydroxide by an alkyl group thus leads to an unexpectedly big increase in basic properties.

The following additional reactions are important when it is required to determine whether a given amine is primary, secondary or tertiary.

1. *Reaction with Nitrous Acid.* The reaction is carried out by adding sodium nitrite to a solution of the amine in excess of hydrochloric acid. The nitrous acid is then liberated in situ and reacts with the amines as follows—

Primary amines—Formation of the alcohol with evolution of nitrogen.

$$R{-}N\boxed{H_2 + O}N{-}OH \rightarrow R{-}OH + N_2 + H_2O$$

Secondary amines—Formation of a nitrosamine (a yellow oil, which may be extracted with ether and purified by steam distillation)—no nitrogen evolution.

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!N\boxed{H + HO}N{=}O \rightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!N{-}NO + H_2O$$

Tertiary amines—Tertiary *aliphatic* amines do not react with nitrous acid—(tertiary *aromatic* amines form nitroso-compounds, for example, $Et_2N{-}C_6H_4{-}NO$).

2. *The Carbylamine Reaction.* This is a very delicate test for a primary amine. When a primary amine is warmed with chloroform and alcoholic potash, the very persistent and offensive odour of an isocyanide (or carbylamine) is obtained. The test should be carried out using only a small quantity of the amine, and once the carbylamine odour has been detected, the tube should be cooled and very carefully treated with an excess of concentrated hydrochloric acid. The latter stops the reaction and destroys the poisonous iso-cyanide.

$$C_2H_5NH_2 + CHCl_3 + 3KOH = 3KCl + 3H_2O + C_2H_5NC$$

Secondary and tertiary amines do not give this reaction.

3. *Reaction with Benzene Sulphonyl Chloride* ($C_6H_5 . SO_2Cl$) or with

benzoyl chloride (C_6H_5 . COCl). In these reactions the hydrogen of the amine is substituted by the group (C_6H_5 . SO_2—) or (C_6H_5 . CO—).

$$R—NH_2 \rightarrow R—NH—OC \,.\, C_6H_5 \text{ (soluble in KOH)}$$

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!NH \rightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!N—OC \,.\, C_6H_5 \text{ (insoluble in KOH)}$$

$$\begin{matrix} R \\ R— \\ R \end{matrix}\!\!>\!N \text{ (contains no hydrogen on the N-atom) no reaction.}$$

Quaternary Ammonium Compounds

These are formed by the "addition" of an alkyl halide (usually the iodide) to the tertiary amine—

$$Et_3N + EtI \rightarrow [Et_4N]I$$

tetra-ethyl ammonium iodide

These quaternary ammonium halides react with moist silver oxide to form the corresponding quaternary ammonium hydroxide, for example, tetra-ethyl ammonium hydroxide—

$$[Et_4N]\,I + Ag\,OH \rightarrow AgI + [Et_4N]OH$$

This is a white deliquescent solid which dissolves readily in water to give a strongly alkaline solution. As a class, the quaternary ammonium hydroxides are strong bases, they absorb carbon dioxide from the air, and have a soapy feel, etc. They decompose on heating to form the tertiary amine and alcohol—

$$[(CH_3)_4N]OH \rightarrow (CH_3)_3N + CH_3OH$$

but more complex compounds break up on heating to form an unsaturated hydrocarbon and water instead of the alcohol—

$$[(C_2H_5)_4N]OH \rightarrow (C_2H_5)_3N + C_2H_4 + H_2O$$

Ascent and Descent in an Homologous Series

It is possible by choosing the appropriate reactions to convert one compound into the next higher member of the homologous series. Thus, methyl alcohol may be converted into ethyl alcohol by the following sequence of reactions—

$$CH_3 \,.\, OH \xrightarrow{P \text{ and } I_2} CH_3 \,.\, I \xrightarrow{KCN} CH_3 \,.\, CN \xrightarrow{H_2O}$$

$$CH_3 \,.\, COOH \xrightarrow{PCl_5} CH_3 \,.\, COCl$$

$$CH_3 \,.\, CHO \xrightarrow{\bar{H}} CH_3 \,.\, CH_2OH$$

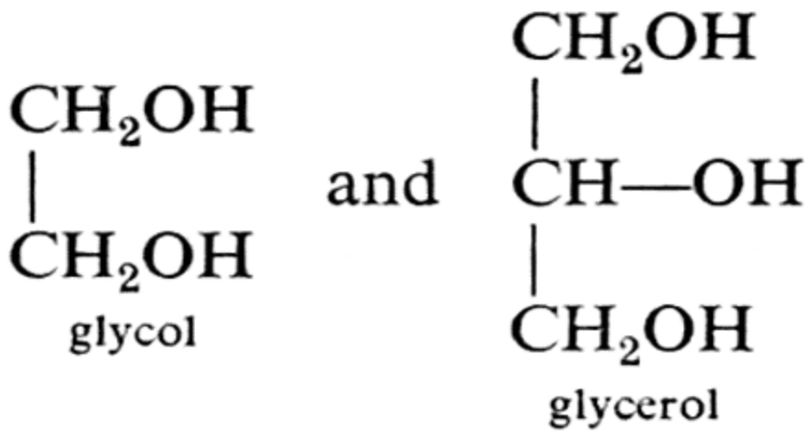
(the $\bar{H}$ also connects $CH_3 \,.\, COCl$ to $CH_3 \,.\, CHO$)

By a different sequence of reactions, it is possible to descend the series. Thus, to convert ethyl alcohol to methyl alcohol the reactions would be—

CHAPTER 34

POLYHYDRIC ALCOHOLS, POLYBASIC ACIDS AND THEIR DERIVATIVES

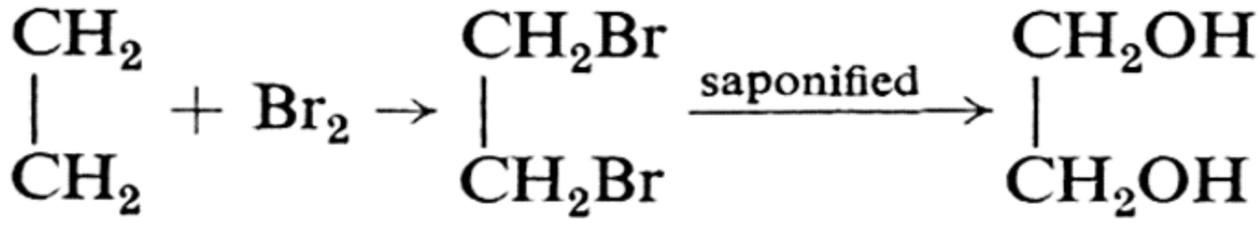
Polyhydric Alcohols. As the name suggests, these are compounds which contain more than one alcoholic group in the hydrocarbon molecule. The simpler and best known examples include—



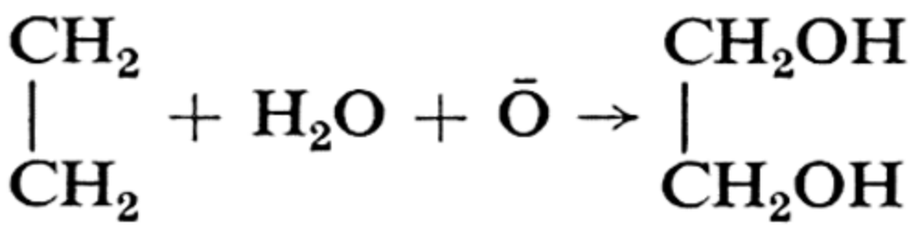
In general, these polyhydric alcohols possess the properties of the monohydric alcohols *n* times, where *n* is the number of hydroxyl groups in the molecule. The characteristic additional properties associated with increasing *n* are: (*a*) increasing boiling point—due to increasing molecular weight, (*b*) increasing solubility in water, and (*c*) increasing sweetness.

The very large class of compounds, known collectively as the sugars, may be regarded as derivatives of the higher polyhydric alcohols.

Glycol (or Ethylene Glycol), $C_2H_4(OH)_2$, may be prepared by boiling ethylene dibromide with sodium hydroxide or sodium carbonate solution—



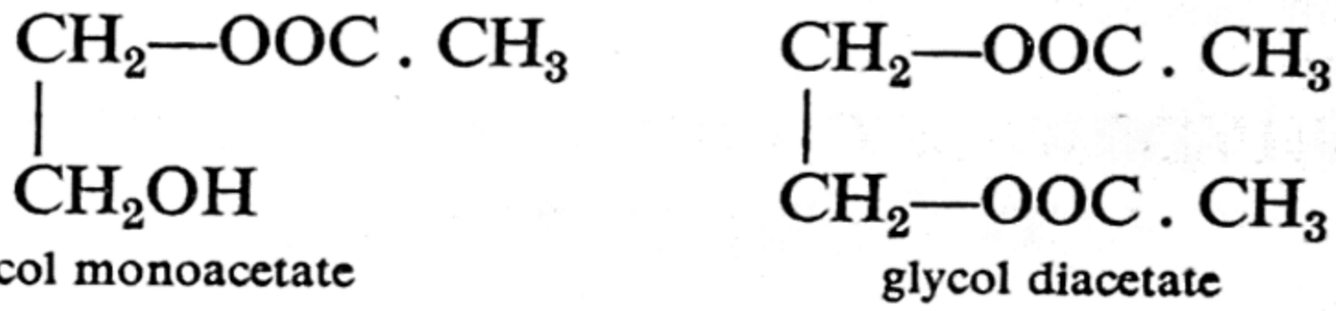
The oxididation of ethylene with a cold, very dilute, alkaline solution of potassium permanganate also gives rise to glycol



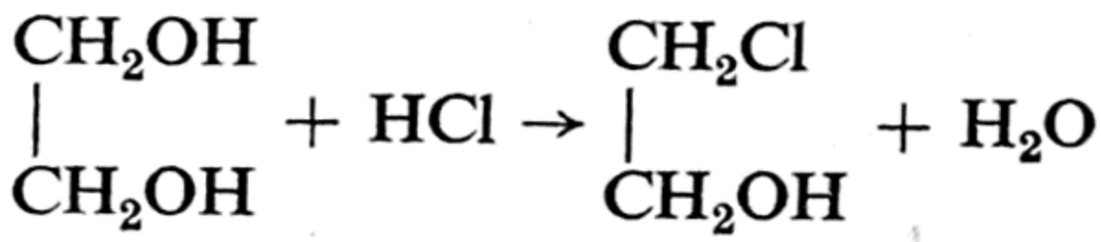
Properties. Glycol is a colourless viscous liquid (b.p. 197°C, density 1·110) with a sweet taste. It is extensively used as an "anti-freeze" in motor-car radiators during cold weather periods. Chemically, its properties are those of the monohydric alcohols two-fold, since it contains

two hydroxyl groups. The more important of these reactions are given below.

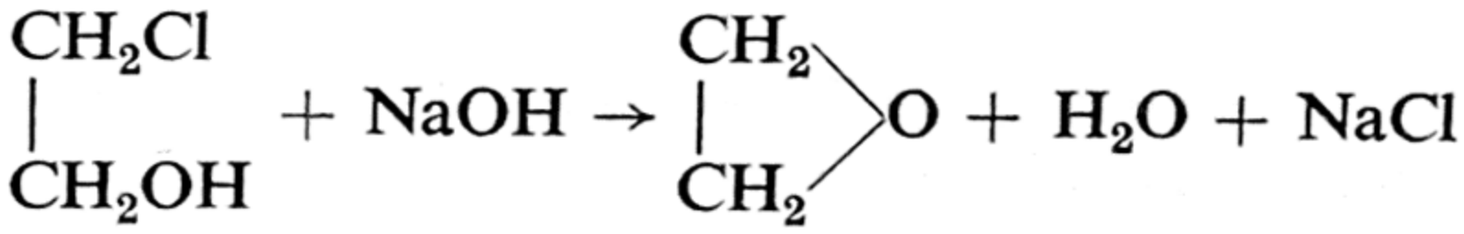
1. Formation of esters with acids. Examples include—



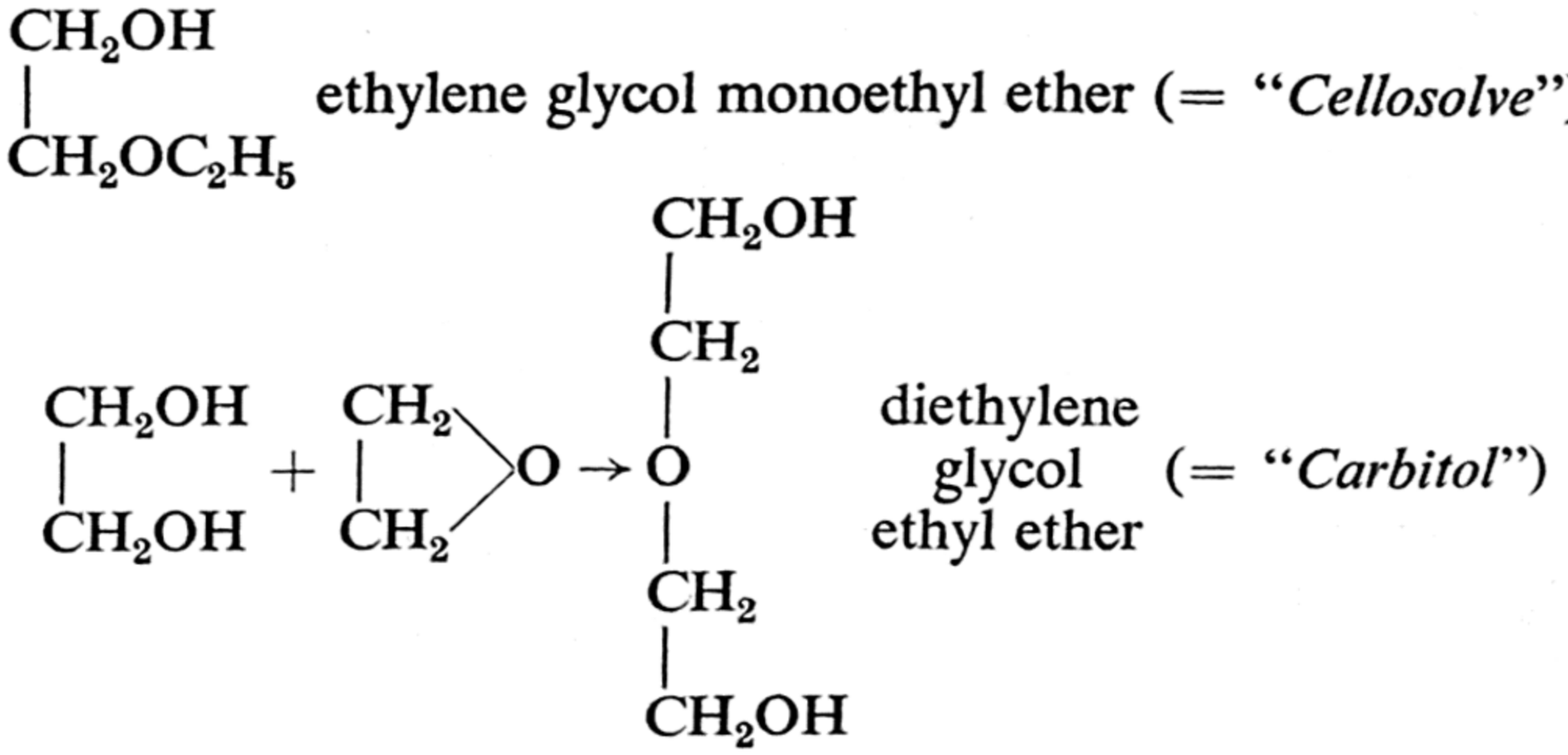
With hydrochloric acid, the reaction stops at the half-way stage to form ethylene chlorhydrin—



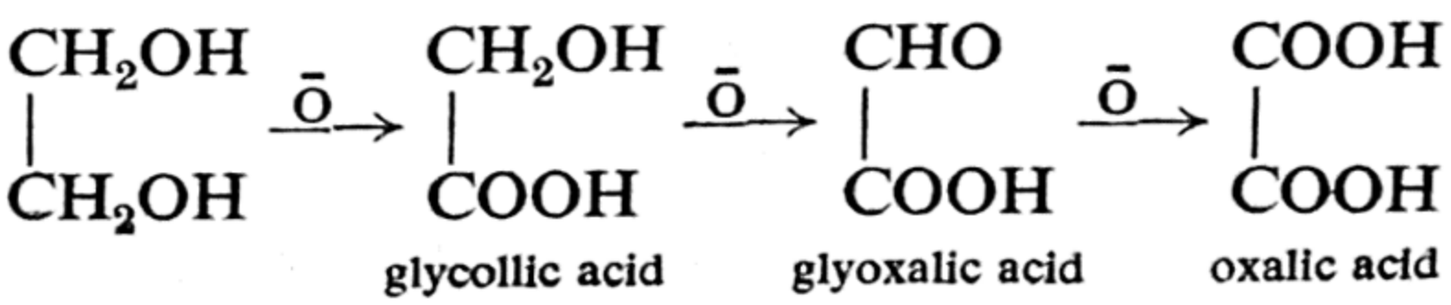
2. The latter compound, when heated with sodium hydroxide, forms ethylene oxide—



Ethylene oxide, which may be regarded as the anhydride of glycol, reacts with alcohols to form an important class of ethers, many of which are valuable commercial solvents. Examples include—



3. On careful oxidation with nitric acid, the following compounds are formed—

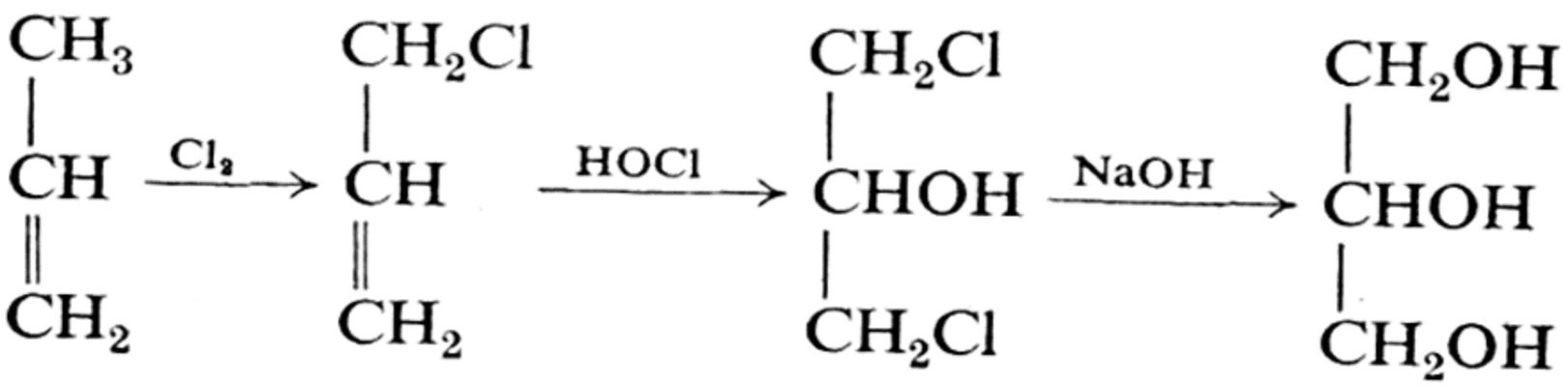


Glycerol (or Glycerine), $CH_2OH . CHOH . CH_2OH$. Glycerol occurs in large quantities in nature as the glycerides of the higher fatty acids in oils and fats (*see* p. 944), and these latter form the most important source of this very important compound.

The recovery of glycerol from the waste soap-lyes, that is the solutions remaining after saponifying fats with sodium hydroxide and salting out the soap, is an important example of the commercial methods for obtaining glycerol from fats. The lyes are first neutralized with hydrochloric acid and then treated with ferric salts to precipitate out any free organic acids present. After filtration, the solution, which may contain from 3–8 per cent of glycerol, is concentrated by evaporation in vacuo. A considerable proportion of the salt (NaCl) separates out during this process and is separated. The solution containing about 80 per cent glycerol (and 10 per cent NaCl) is then distilled under reduced pressure in a current of superheated steam to produce chemically pure glycerol. Anhydrous glycerol is obtained from this by vacuum evaporation.

A similar sequence of operations is employed to separate glycerol from the sweet liquors obtained on "splitting" oils and fats (for example, by Twitchell Reagents, or steam heating, or heating with a small quantity of lime, etc.).

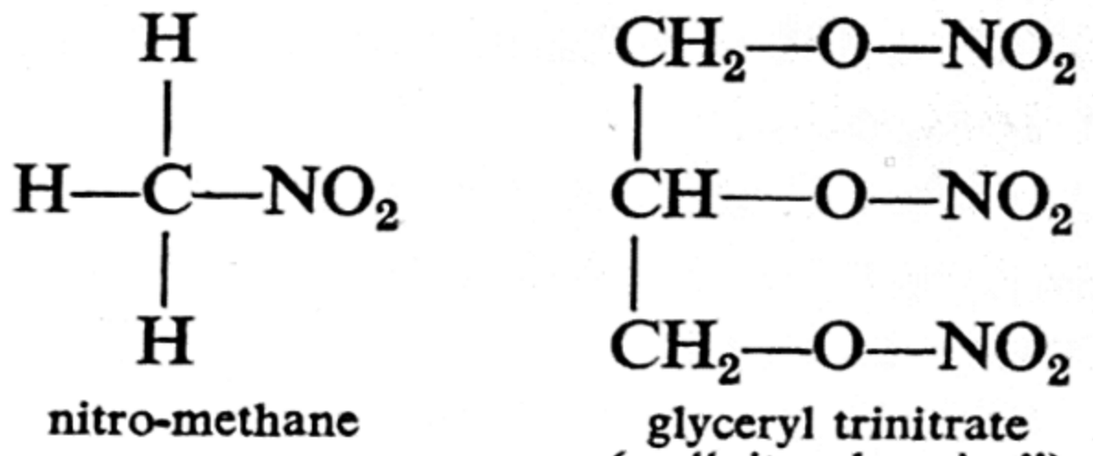
Glycerol is also produced commercially, particularly in the U.S.A., by synthetic methods from propylene. Propylene, obtained as a by-product of the cracking process to convert higher petroleum oils into petrols, is converted into glycerol by the following reactions—



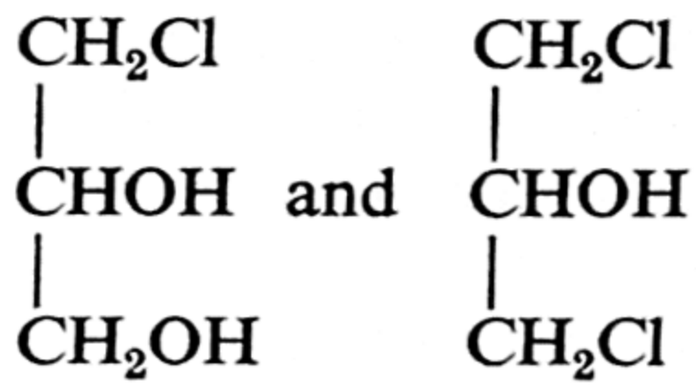
Properties. Glycerol is a colourless syrupy liquid which is very hygroscopic and mixes with water in all proportions. It is used in large quantities in the manufacture of nitro-glycerine explosives, and in smaller quantities in the manufacture of glyptal resins (made by reaction with phthalic anhydride), and in paint and varnish manufacture; as an anti-freeze in motor-cars; as a softening and moistening agent in printing inks, typewriter ribbons, leather goods, tobacco; and in many pharmaceutical and food products.

Chemically, its properties are those to be expected for a tri-hydric alcohol. Thus, it forms mono-, di- and tri-esters, which are known as glycerides. *Nitro-glycerine* is the triglyceride formed by reaction with nitric acid. It should, however, be called glyceryl tri-nitrate since it does not contain a nitro (NO_2) group directly attached

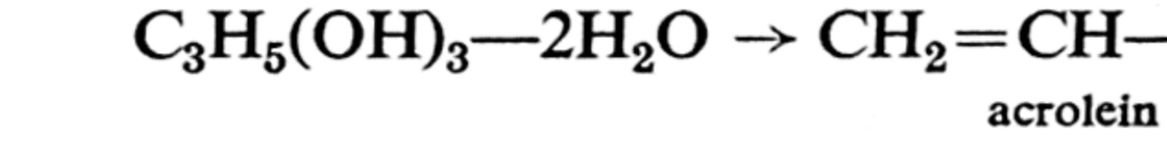
through the N atom to a carbon atom and is therefore not a nitro-compound—



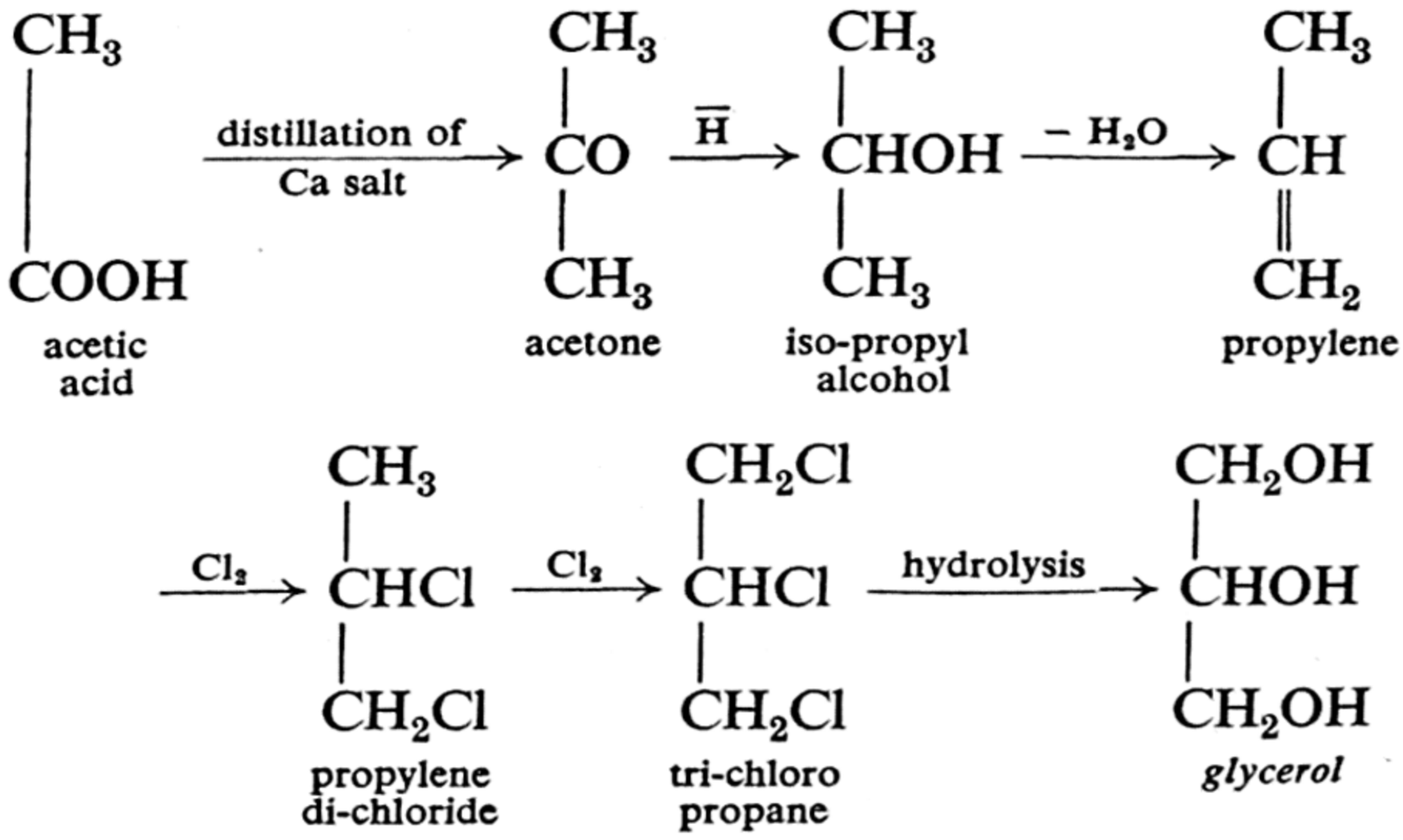
With hydrochloric acid, glycerol forms only the mono- (α-) and di- ($\alpha\alpha'$-) esters—



When heated with dehydrating agents, an unsaturated aldehyde, known as acrolein is formed—



Formula. The formula of glycerol, which may be established by methods analogous to those outlined for methyl alcohol (*see* p. 894), receives elegant confirmation from the following synthesis of glycerol from acetic acid—



DI-BASIC ACIDS

Oxalic Acid, $\begin{matrix}\text{COOH}\\|\\\text{COOH}\end{matrix}$, the simplest of the dibasic organic acids, is present in many vegetable substances, such as the leaves of rhubarb and beet

plants. It is, however, prepared commercially from raw materials which do not themselves contain oxalic acid, for example, saw-dust, and also by synthetic methods from carbon monoxide.

1. *From Sawdust.* The sawdust is fused with sodium hydroxide in presence of air. Oxalic acid is formed as its sodium salt, and this is extracted with water. The solution of sodium oxalate is then treated with milk of lime to precipitate calcium oxalate. This latter is then separated and treated with the calculated quantity of dilute sulphuric acid. The solution of oxalic acid which results is filtered from the calcium sulphate, and concentrated by evaporation. Oxalic acid crystallizes as the di-hydrate, $H_2C_2O_4 \cdot 2H_2O$.

2. *From Sugar.* When sugar is added to concentrated nitric acid heated on a water bath, a vigorous reaction occurs to form oxalic acid. Concentration of the solution by evaporation then produces crystals of oxalic acid di-hydrate.

3. *From Carbon Monoxide.* Carbon monoxide is first made to react with 97–98 per cent sodium hydroxide solution at 200°C under 8–10 atmospheres pressure in an autoclave to form sodium formate—

$$CO + NaOH = H \cdot COONa$$

The temperature is then raised to about 375°C and the pressure in the autoclave reduced to draw off the hydrogen produced by the following decomposition of the sodium formate—

$$2H \cdot COONa \rightarrow \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2$$

When no more hydrogen is evolved, milk of lime is added to precipitate calcium oxalate, which is separated and treated with sulphuric acid as in the first method—

$$Na_2C_2O_4 + Ca(OH)_2 \rightarrow CaC_2O_4 + 2NaOH$$

Properties. Oxalic acid crystallizes from aqueous solution as the dihydrate, $H_2C_2O_4 \cdot 2H_2O$, m.p. 101°C. The anhydrous acid may be prepared by carefully heating this dihydrate, but more vigorous heating leads to decomposition as indicated in the following reactions—

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \rightarrow H \cdot COOH \text{ (formic acid)} + CO_2$$

$$\rightarrow H_2O + CO$$

Similar decomposition occurs on heating the oxalate salts. Thus calcium oxalate decomposes to form calcium carbonate and carbon monoxide—

$$CaC_2O_4 \rightarrow CaCO_3 + CO$$

The formation of formic acid by thermal decomposition of oxalic acid explains the fact that whereas formic acid will reduce alkaline permanganate in the cold, oxalic acid will only do so slowly on heating. With acidified permanganate, however, the reaction occurs on gently warming. This reaction occurs quantitatively, so that oxalic acid is often used to standardize permanganate solutions in volumetric analysis—

$$H_2C_2O_4 + \bar{O} \rightarrow 2CO_2 + H_2O$$

The oxalic acid solution, prepared by dissolving a weighed amount of oxalic acid di-hydrate in water, is acidified with excess dilute sulphuric acid and heated to about 70°C before adding the permanganate solution from the burette. The permanganate is decolourized, and the endpoint of the titration is determined in the usual way by the first appearance of a permanent pale-pink coloration.

Oxalic acid (and oxalates) are decomposed on heating with concentrated sulphuric acid to liberate carbon dioxide and carbon monoxide—

$$H_2C_2O_4—H_2O \rightarrow CO + CO_2$$

This latter reaction may be used as a test for oxalic acid (or oxalates). The carbon monoxide burns with a blue flame, and the carbon dioxide may be detected by the lime-water reaction. Other polybasic organic acids also liberate carbon monoxide and carbon dioxide on heating with concentrated sulphuric acid, but these are distinguished by blackening of the solution due to charring, by odour, etc.

Compound	Observation
Cyanide, oxalate, formate .	Carbon monoxide evolved—no charring
Tartrate or sugars . . .	Chars rapidly, carbon monoxide evolved and odour of burnt sugar
Malate	Chars rapidly, carbon monoxide evolved and odour of apples
Citrates and succinates . .	Chars slowly, carbon monoxide evolved and irritant vapours

Oxalic acid (and oxalates) may also be detected by reaction with calcium chloride in neutral solution. A white precipitate of calcium oxalate is formed which is insoluble in dilute acetic acid, but dissolves in dilute hydrochloric acid.

The other reactions of oxalic acid are those to be expected from a di-basic organic acid. Thus it forms both normal and acid salts, known as oxalates, by reaction with bases; it forms esters, for example, by distilling the anhydrous acid with the appropriate alcohol; and it reacts with phosphorus pentachloride to form oxalyl chloride—

$$\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow{+\ PCl_5} \begin{matrix}COCl\\|\\COCl\end{matrix}$$

Oxamide, the di-amide, may be prepared by heating ammonium oxalate, or better by adding strong ammonia to methyl or ethyl oxalate, when it is obtained as a white precipitate—

$$\begin{matrix}COOCH_3\\|\\COOCH_3\end{matrix} + 2NH_3 \rightarrow \begin{matrix}CO\ .\ NH_2\\|\\CO\ .\ NH_2\end{matrix} + 2CH_3OH$$

When oxamide is heated with phosphorus pentoxide, the corresponding nitrile, known as cyanogen, is formed—

$$\begin{matrix}CO\ .\ NH_2\\|\\CO\ .\ NH_2\end{matrix} \rightarrow \begin{matrix}CN\\|\\CN\end{matrix} + 2H_2O$$

Uses. Oxalic acid, potassium hydrogen oxalate (*salts of sorrel* or *salts of lemon*) and potassium quadroxalate are used in the textile industries, particularly in calico printing, and also for removing colour (i.e. a bleaching agent), ink stains, iron mould and for cleaning leather. Both the acid and its salts are very poisonous. Potassium quadroxalate is a double salt of potassium hydrogen oxalate and oxalic acid, and has the formula $KHC_2O_4\ .\ H_2C_2O_4\ .\ 2H_2O$.

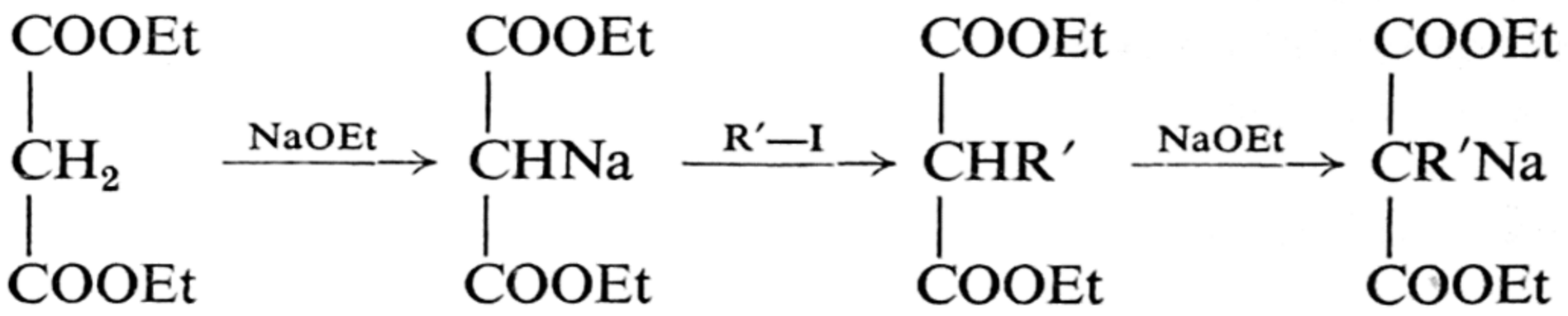
Malonic Acid, $\begin{matrix}COOH\\|\\CH_2\\|\\COOH\end{matrix}$. Malonic acid, the next higher homologue to oxalic acid, may be prepared from acetic acid by the following reactions—

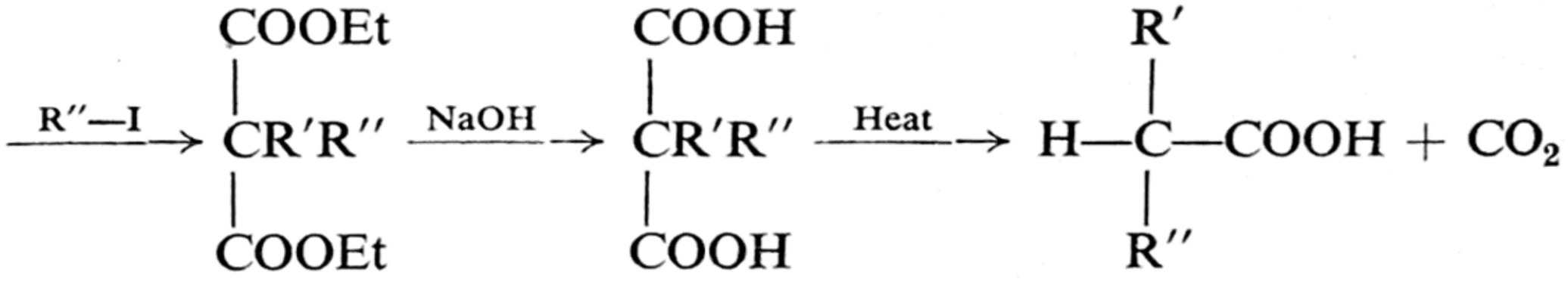
$$CH_3\ .\ COOH \xrightarrow{Cl_2} CH_2Cl\ .\ COOH \xrightarrow{KCN}$$

$$CH_2\begin{matrix}\diagup CN\\\diagdown COOH\end{matrix} \xrightarrow{\text{hydrolysis}} CH_2\begin{matrix}\diagup COOH\\\diagdown COOH\end{matrix}$$

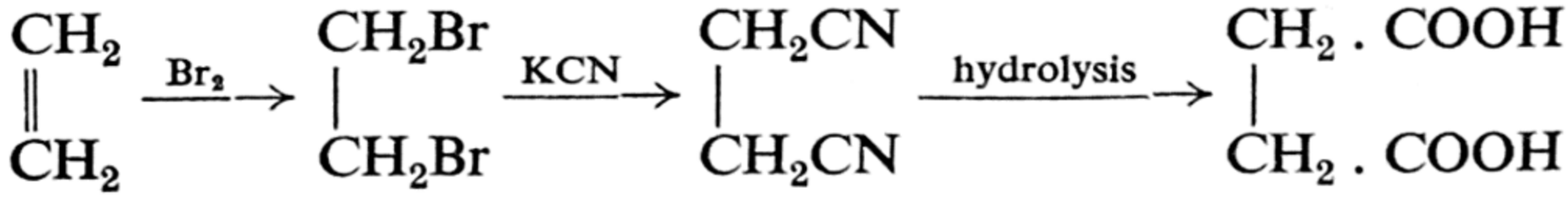
When heated, malonic acid loses carbon dioxide to form acetic acid. This reaction is used in the *malonic-ester synthesis* for preparing derivatives of acetic acid.

Malonic-ester Synthesis. The —CH_2— group in malonic acid possesses feeble acidic properties. In the free acid, however, these properties are completely masked by the much more strongly acidic —COOH groups. When malonic acid is converted into one of its esters, such as di-ethyl malonate, the acidic properties of the —CH_2— group become apparent. This fact is utilized in the so-called malonic-ester synthesis of substituted acetic acids, as in the following example—





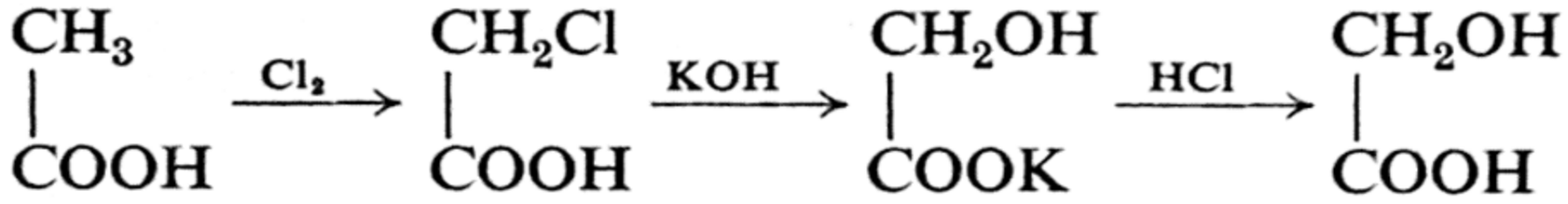
Succinic Acid, $\begin{matrix} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{matrix}$. The following preparation of succinic acid from ethylene serves also to establish the formula of this acid—



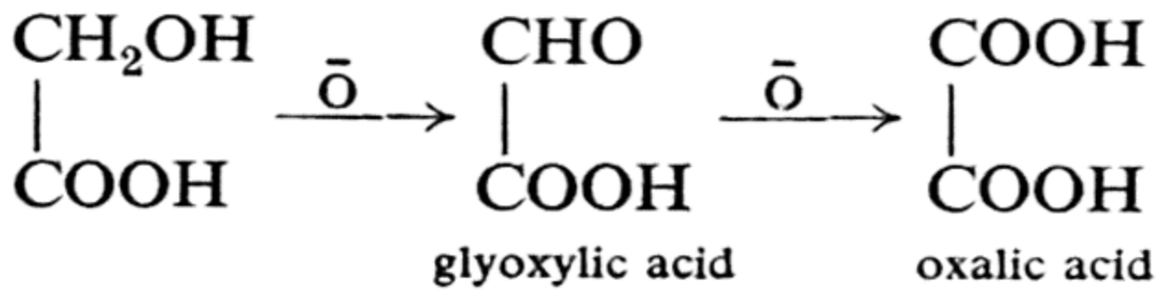
HYDROXY-ACIDS

Glycollic Acid, $\begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}$. This acid, known also as hydroxy acetic acid, may be prepared from acetic acid by the intermediate formation of mono-chloroacetic acid, $CH_2Cl \cdot COOH$. Chlorine is bubbled into hot acetic acid in the presence of a halogen carrier, such as iodine. Reaction occurs to form mono-, di- and tri-chloroacetic acids, the course of the substitution being followed by weighing the reaction vessel from time to time. When the increase in weight corresponds approximately to the formation of mono-chloroacetic acid, the reaction is stopped and the mono-chloroacetic acid separated by fractional distillation. It is then converted into potassium glycollate by boiling with aqueous potassium hydroxide. Glycollic acid is

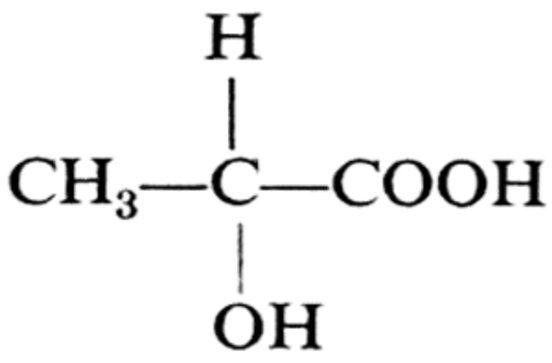
then obtained by boiling the potassium salt with dilute hydrochloric acid, evaporating to dryness and extracting the glycollic acid with acetone.



Glycollic acid is a crystalline substance, melting at 80°C. It possesses the properties both of an alcohol and of a monobasic acid. This is confirmed by its reactions with phosphorus pentachloride, alcohols, alkalis, etc. On oxidation, it is oxidized to glyoxylic acid and to oxalic acid—



Lactic Acid, $CH_3 . CH(OH) . COOH$, i.e.

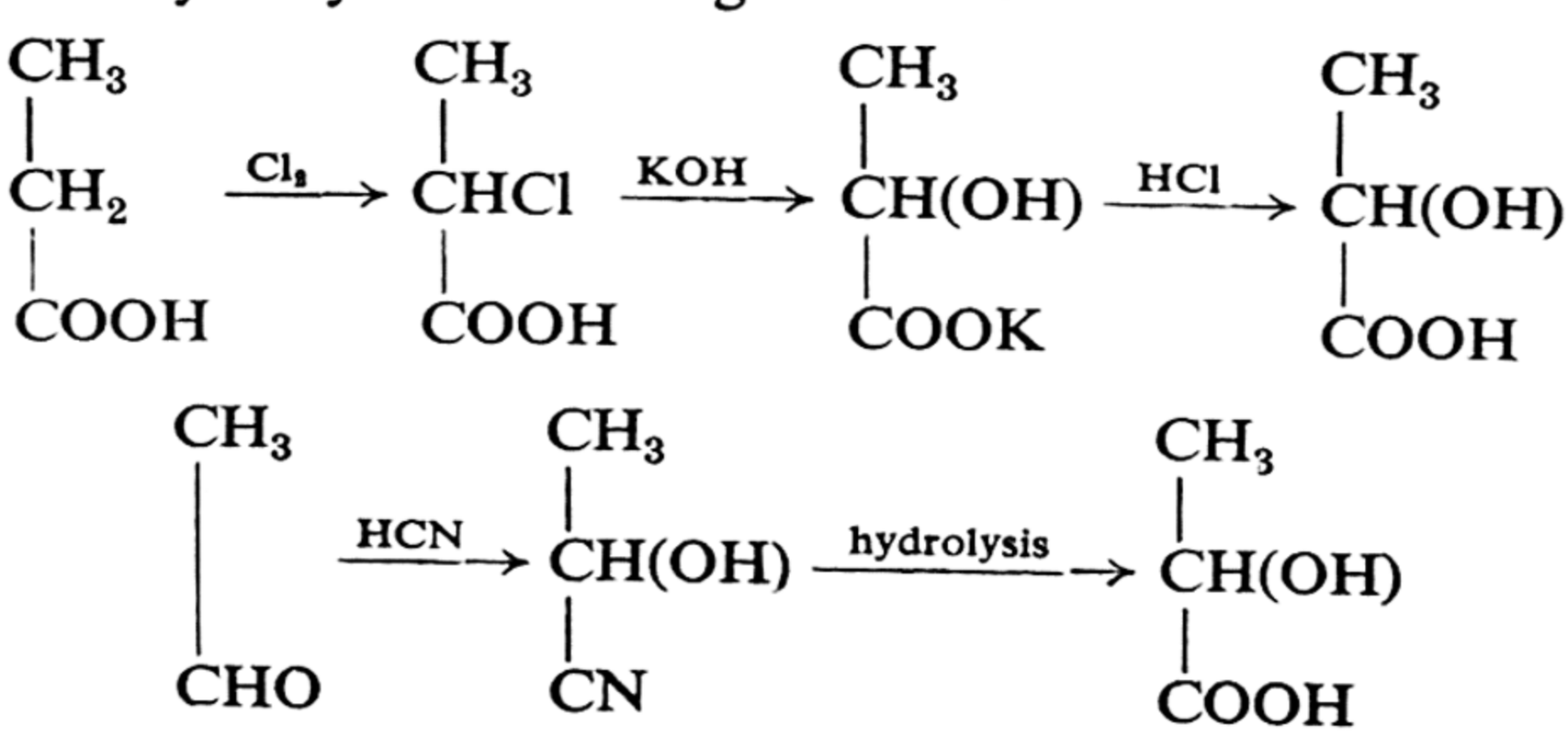


Lactic acid occurs in sour milk, and results from the fermentation of milk sugar (lactose). It is prepared commercially by the controlled lactic fermentation of sugars from molasses or of the lactose in milk whey.

$$C_6H_{12}O_6 \rightarrow 2CH_3.CH(OH).COOH$$

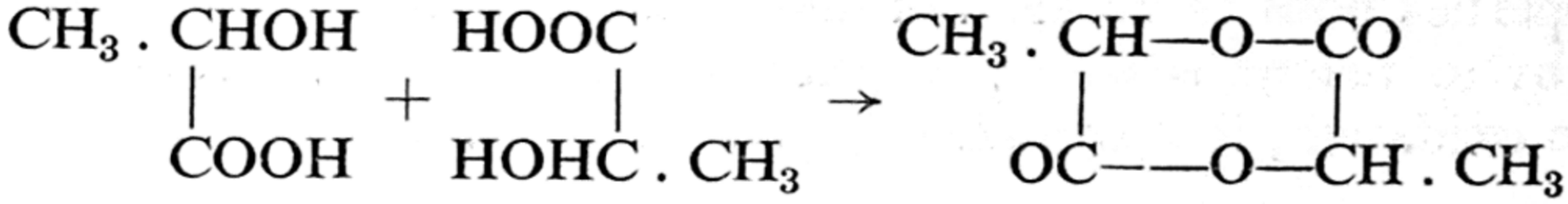
Its principal uses are as a de-liming agent in tanning (calcium lactate is soluble in water), and in the acid-dyeing of wool. Smaller quantities are used as its esters, ethyl and butyl lactate (used as lacquer solvents and plasticizers), as calcium lactate (for medicinal use), and as the acid in many pickles and soft drinks.

Lactic acid may also be prepared synthetically from propionic acid and from acetaldehyde by the following reactions—

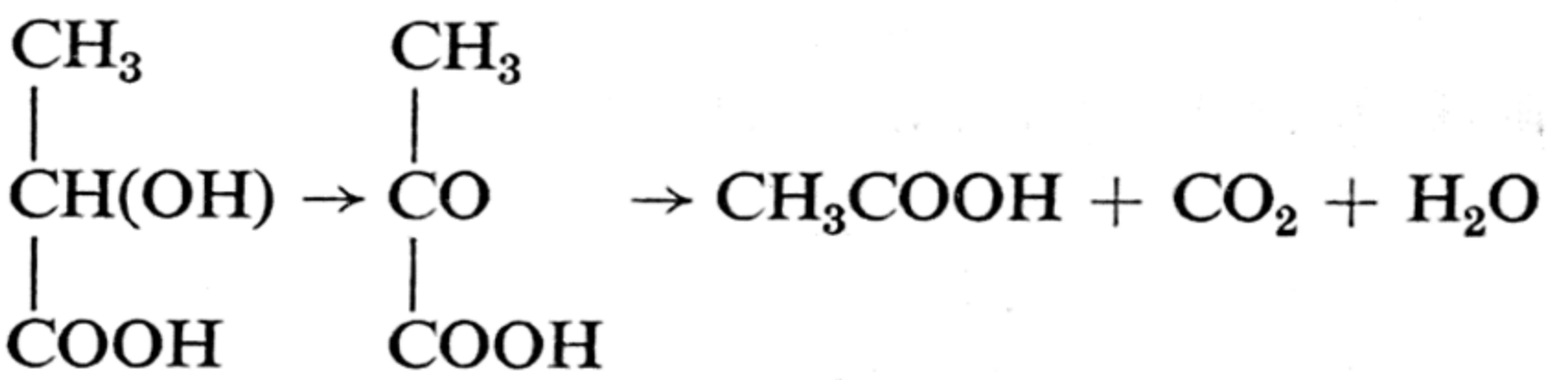


Properties of Lactic Acid. As usually obtained, it is a thick sour liquid, but when pure it is crystalline and melts at 18°C. It is both a monocarboxylic acid and also a secondary alcohol, and accordingly shows the reactions of both these classes of compounds. The following additional reactions should be noted.

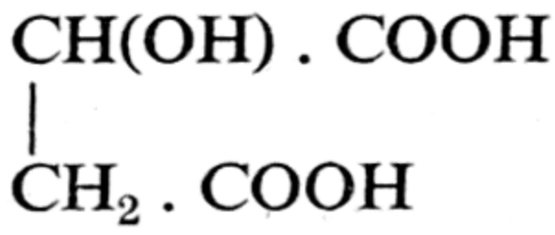
When lactic acid is heated it forms a cyclic double ester with itself, known as Lactide—



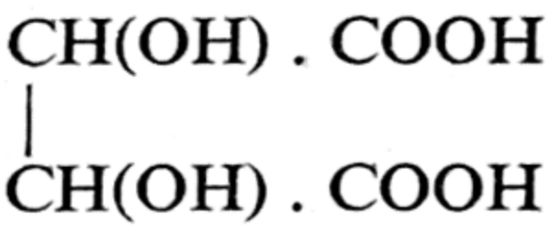
Mild oxidation converts lactic acid into pyruvic acid, and the latter under more vigorous oxidizing conditions is decomposed to form acetic acid—



Malic Acid. This is the mono-hydroxy derivative of succinic acid and has the formula



Tartaric Acid. This is the di-hydroxy derivative of succinic acid, and is particularly interesting because of the part it played in the development of the theory of stereoisomerism (*see* p. 967). It has the formula



It is one of the more common vegetable acids, and is obtained commercially from grapes during fermentation. A deposit of impure potassium hydrogen oxalate, known as *argol*, is deposited. The pure potassium hydrogen oxalate, known as *cream of tartar*, is obtained by leaching with water, filtering and crystallizing the solution. It may be converted into tartaric acid by treatment with sulphuric acid, but the usual procedure is to treat the argol deposit. This is boiled with hydrochloric acid and then nearly neutralized with milk of lime to precipitate calcium tartrate. The filtrate is treated with calcium chloride to obtain a further deposit of calcium tartrate. The combined deposits of calcium tartrate are then treated with the calculated quantity of dilute sulphuric acid, to precipitate calcium sulphate and produce an aqueous solution of tartaric acid. This is filtered off and evaporated to crystallize the tartaric acid.

Tartaric acid may be prepared in the laboratory from succinic acid by the following reactions—

$$\begin{array}{l} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{array} \xrightarrow{Br_2} \begin{array}{l} CHBr \cdot COOH \\ | \\ CHBr \cdot COOH \end{array} \xrightarrow{AgOH} \begin{array}{l} CH(OH) \cdot COOH \\ | \\ CH(OH) \cdot COOH \end{array}$$

Properties and Uses. Tartaric acid is a di-hydroxy di-carboxy acid. and shows the usual reactions characteristic of these groups. When heated, tartaric acid (and tartrates) begins to decompose near its melting point (about 167°C) and chars when strongly heated producing the familiar odour of burnt sugar. The same odour is noticed when tartaric acid is heated with concentrated sulphuric acid. In this case the tartaric acid chars rapidly and is accompanied by evolution of carbon monoxide (blue flame) and carbon dioxide (lime-water test). Tartaric acid also gives the silver-mirror test with ammoniacal silver nitrate.

Tartaric acid is used in baking powders, and in many effervescent drinks, such as health salts and Seidlitz powders. *Rochelle salts*, used in Fehling's solution, is sodium potassium tartrate. *Tartar emetic* obtained on boiling cream of tartar with antimony oxide and water, is potassium antimonyl tartrate.

STEREOISOMERISM AND OPTICAL ACTIVITY

It was stated in the last section that tartaric acid played an important part in the discovery and explanation of the phenomenon of stereoisomerism. But to understand fully all the implications of stereoisomerism, it is necessary to discuss first the phenomenon of optical activity.

Stated briefly, a substance is optically active if it rotates the plane of polarization of plane-polarized light. Ordinary light may be considered on the wave theory as energy transmitted through space by a wave-like motion, in which each ray is considered to be vibrating perpendicularly to its direction of propagation. The analogy of the waves produced by dropping a stone into a still pond is very appropriate, especially if one remembers the way in which a floating object, such as a cork, moves vertically up and down as the wave-motion spreads out from the point at which the stone entered. The rays of light also vibrate perpendicularly to the direction of the ray, but whereas the cork vibrates only up and down, the rays of light vibrate in any direction in the plane perpendicular to the direction of the ray. When, however, light is passed through a Nicol prism, it becomes plane polarized, that is, the rays are now all vibrating in the same plane and the analogy with the cork is complete. Certain substances possess the property of rotating this plane of polarization and are said to be optically active.

An examination of optically-active crystals shows that they do not possess a plane of symmetry, that is, they are *asymmetric*. Some of these

crystals lose their optical activity when they are dissolved and in such cases it may be presumed that the optical activity of the solid results from an *asymmetrical packing* of the molecules in the solid crystal-lattice. Other crystals, however, retain their optical activity in solution, and in these cases the only possible explanation of the phenomenon appears to be that the *molecules themselves* are asymmetric.

We may now consider, briefly, the work of Pasteur on tartaric acid (1848–1854). Tartaric acid, as obtained from the juice of grapes, is optically active. A second compound with the same formula, structure and chemical properties as tartaric acid was subsequently isolated. This compound, now known as racemic acid, differed from tartaric acid only in one respect, namely, it was optically inactive. From these two acids Pasteur prepared crystals of their sodium ammonium salts, $C_4H_4O_6NaNH_4 . 4H_2O$. The one from tartaric acid was found to be optically active, whilst the other from racemic acid was optically inactive. Pasteur, however, noticed that, whereas the crystals of the salt from tartaric acid all had the same arrangement of the crystal faces, the crystals of the salt from racemic acid could be divided into two types depending on the arrangement of certain small faces (shown shaded in the accompanying diagram).

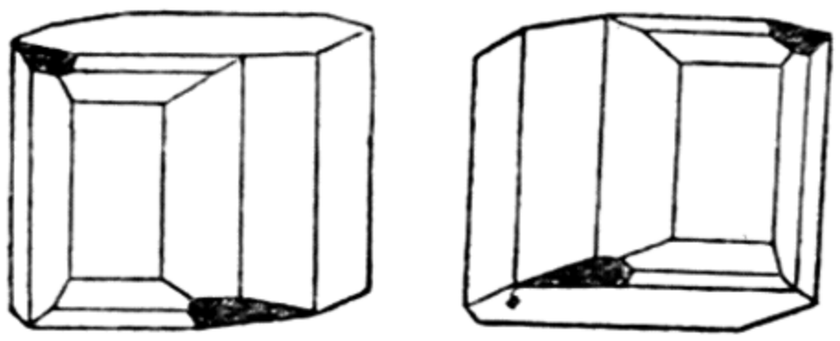
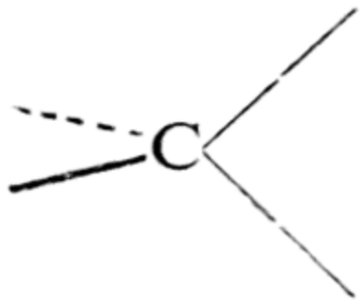


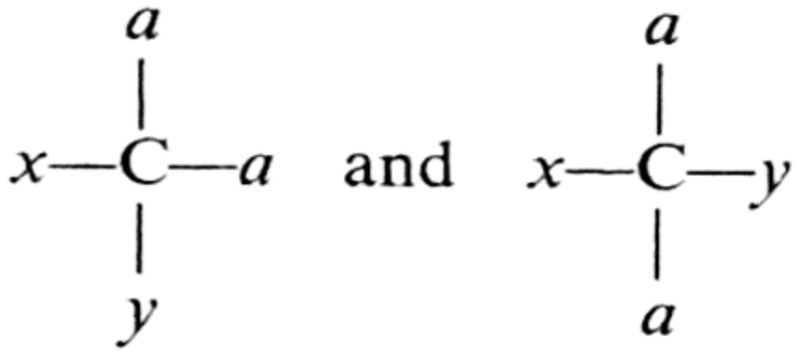
FIG. 269. Sodium Ammonium Tartrate Enantiomorphs

These two crystals are not superposeable, but are such that one is the mirror image of the other. Such crystals are said to be *enantiomorphous*. One of these was identical with the salt obtained from tartaric acid. Pasteur then separated these two forms of the salt from racemic acid and examined their solutions for optical activity. They were both found to be optically active, one rotating the plane of polarization of plane-polarized light to the right (i.e. dextro-rotatory) and the other to the left (i.e. laevo-rotatory). From these two solutions, Pasteur obtained the corresponding acids, and found that one was identical in every respect to the tartaric acid obtained from grapes, whilst the other differed only in that it rotated the plane of polarization to the left. With solutions of equal concentration, the rotation was numerically the same in the two cases, except that one was dextro-rotatory (like tartaric acid from grapes), whilst the other was laevo-rotatory. Pasteur thus established the existence of three forms of tartaric acid, two of which are optically active (*d*— and *l*— tartaric acids) and the third inactive (racemic acid). The latter appeared to be a physical mixture of equal quantities of the *d*— and *l*— tartaric acids and could by suitable methods be separated (or "resolved") into these two acids. A fourth form of tartaric acid, known as meso-tartaric acid, was subsequently discovered. This form is also optically inactive, but unlike racemic acid, it cannot be resolved into the two active acids.

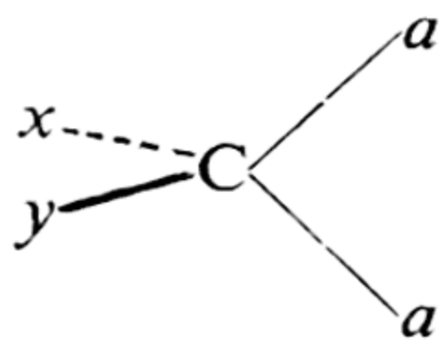
The explanation of these various forms of tartaric acid followed quickly on the suggestion made independently by van't Hoff and Le Bel in 1874, that the four valency bonds of carbon are not planar, as was previously supposed, but have a regular spatial distribution. The carbon atom may be regarded as being at the centre of a regular tetrahedron with its four valency bonds directed towards the four corners, as in the diagram.



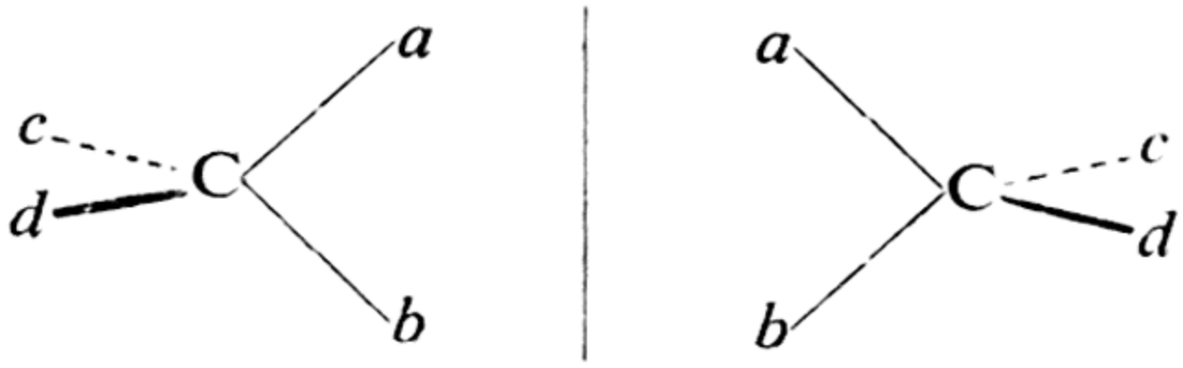
Some such theory was necessitated by the fact that only one compound having the formula of the type Ca_2xy, for example ($CH_2(OH) . COOH$), has ever been isolated, whereas, if the planar arrangement of the carbon bonds is correct, there should be two—



With a regular tetrahedral arrangement of the carbon bonds, however, this difficulty disappears, since only one formula is possible—

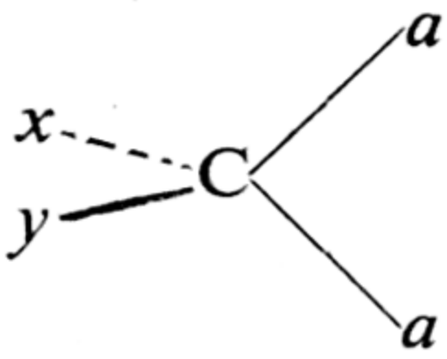


On this theory, however, compounds of the type *Cabcd*, in which the carbon atom is directly united to four different atoms or groups, should exist in two forms which are not superposeable but such that one is the mirror image of the other, e.g.—

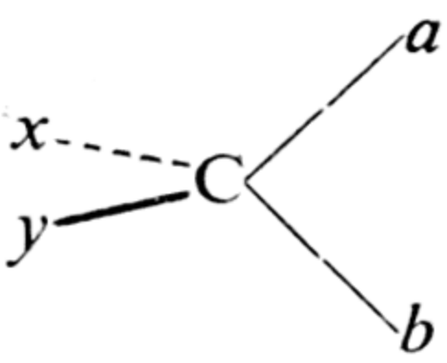


Van't Hoff argued that optical activity results from asymmetry in the molecule of the type described above, and that a compound to be optically

active must contain an *asymmetric carbon atom*, that is, one which is directly linked to four different atoms or groups. It may not be obvious, but it can soon be shown by the use of space models, that this asymmetry results from the absence of a plane (or centre) of symmetry in the molecule—

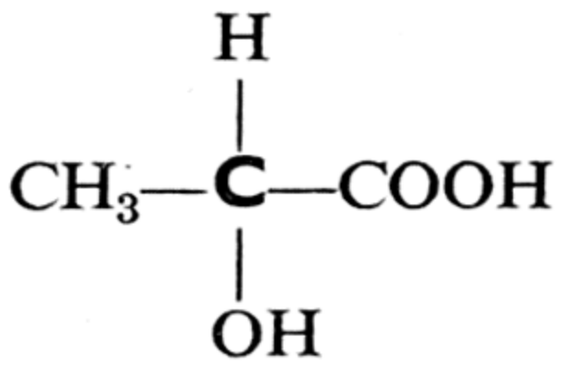


Plane of symmetry perpendicular to the plane of the paper.
Molecule optically *inactive*.

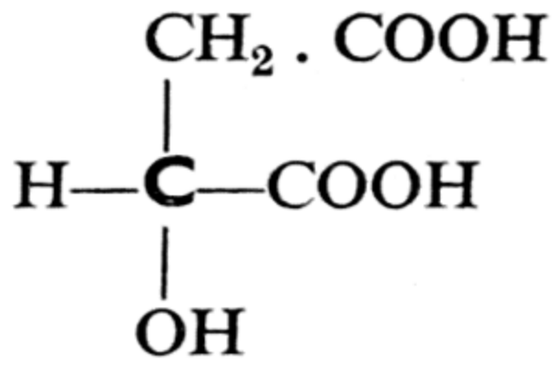


No plane or centre of symmetry.
Molecule optically *active*.

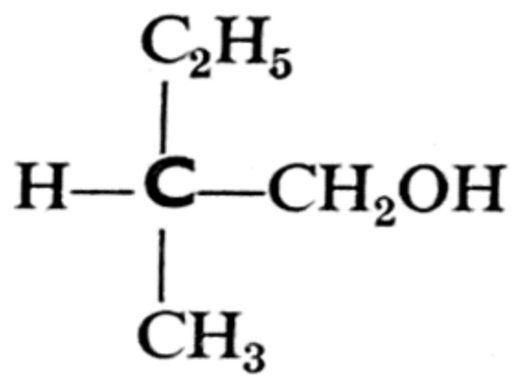
We may, therefore, recapitulate at this stage and say that to be optically active a compound must not possess a plane (or centre) of symmetry. Examples include—



lactic acid



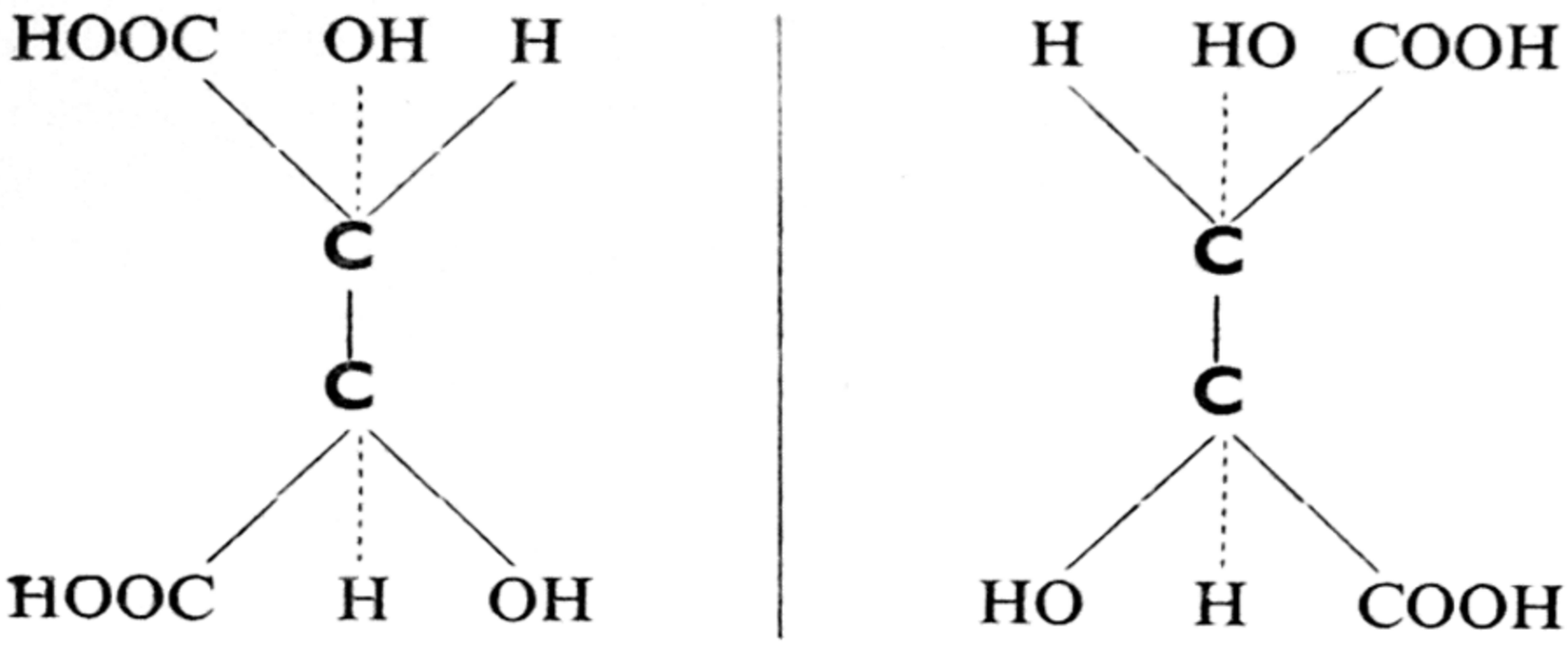
malic acid



amyl alcohol

In each of these compounds, the carbon shown in heavy type is asymmetric. Each exists in three forms, namely dextro-rotatory (*d*—), laevo-rotatory (*l*—) and the inactive racemic form which is an equi-molecular mixture of the *d*— and *l*— forms. Optical activity, however, is not limited to carbon compounds, but is found in covalent compounds of other elements, such as sulphur, nitrogen, tellurium, etc., the necessary condition in every case being the absence of a plane or centre of symmetry.

We are now in a position to discuss the four forms of tartaric acid discovered by Pasteur. Reference to the following space formulae shows that I and II do not possess either a plane or centre of symmetry and must therefore be optically active—they are not superposeable and are such that one is the mirror image of the other. (Make space models of these two forms and show, by rotating one of the asymmetric carbon atoms about the C—C bond, that it is impossible to produce an arrangement in which the molecule possesses either a plane or centre of symmetry.)

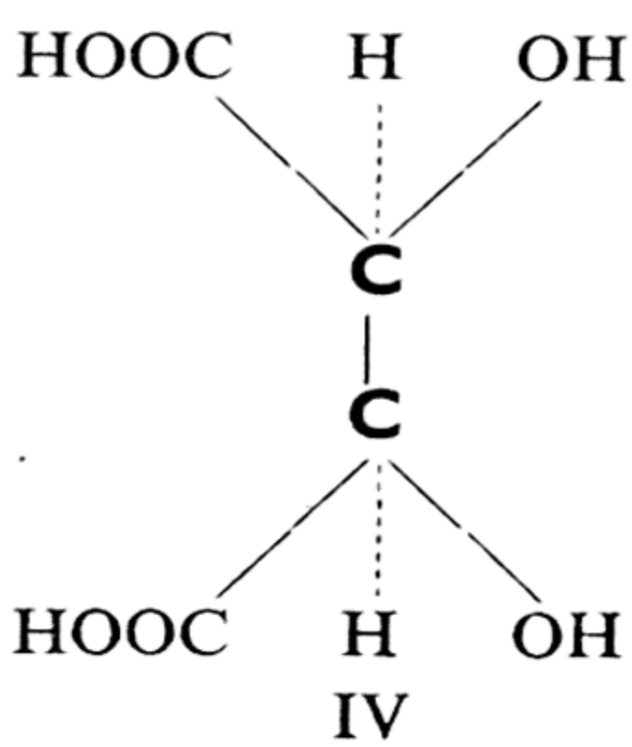


I *mirror* II

Each molecule contains two identical asymmetric carbon atoms (shown in heavy type), but, as we shall see in a moment, this by itself is not sufficient for the molecule to be optically active. If we call the first of these two forms dextro-tartaric acid, then formula II will be that of laevo-tartaric acid. It has not been possible to determine which structure should be assigned to each acid, and so the convention has been adopted in which the dextro-acid is represented by the formula having the lower hydroxyl group to the right of the carbon chain.

Racemic acid, the third form of tartaric acid, is an equi-molecular mixture of these two active forms, and is accordingly said to be *optically inactive by external compensation.*

The fourth form of tartaric acid, namely, meso-tartaric acid, has the following structural formula IV.



IV

In this form, although the molecule possesses two asymmetric carbon atoms, their effects cancel each other; the molecule is said to be *optically inactive by internal compensation.* The molecule in fact possesses a plane of symmetry, as may easily be shown by constructing a space model and rotating one of the asymmetric carbon atoms about the C—C bond. Meso-tartaric acid must, therefore, be optically inactive. It should be particularly noted that in this acid the loss of optical activity results from the internal arrangement in *each* molecule of two *identical* asymmetric carbon atoms, as a result of which the molecule possesses a plane of symmetry. Such a molecule clearly cannot be resolved into *d*— and *l*— active forms.

The four forms of tartaric acid all have identically the same chemical properties. The *d*— and *l*— forms also have the same physical properties with the single exception of their optical activity. A solution of *l*— tartaric acid rotates the plane of polarization of plane-polarized light to the left by the same amount that a solution of *d*— tartaric acid of the same concentration rotates the plane of polarization to the right. Both the racemic acid and meso-tartaric acid are inactive, and each shows slightly different properties (e.g. melting point, solubility, etc.) from the two active forms. The racemic acid, however, is optically inactive by external compensation, and so may be resolved into *d*— and *l*— forms; but the meso-acid, which is inactive by internal compensation may not be resolved.

Resolution of Racemic Acid and Racemic Mixtures. The term *racemate* is now applied in a general sense to all cases of compounds which are optically inactive by external compensation. We must distinguish, however, between the following three possible forms of an externally compensated, optically inactive, compound—

(*a*) A mixture of the *d*— and *l*— forms, referred to as a *dl*—mixture.

(*b*) A compound of the *d*— and *l*— forms, referred to as a racemate or racemic compound.

(*c*) A solid solution (i.e. mixed crystals) of the *d*— and *l*— forms, referred to as a pseudo-racemate.

Pasteur's Three Methods for Resolving Racemic Mixtures

1. *Crystal Form Method.* Below 26°C, sodium ammonium racemate crystallizes as a racemic mixture (i.e. *dl*—mixture), and the two enantiomorphous forms may then be separated by examining each crystal separately under the microscope. This method is not very important since very few compounds crystallize as *dl*— mixtures, and the process is moreover somewhat tedious and dependent upon the formation of well-defined crystals.

2. *Chemical Method.* The principle of this method is to fractionally crystallize the salt formed by neutralizing the externally compensated acid (or base) with an optically active compound.

$$dl\text{—acid} + l\text{—base} \rightarrow \begin{cases} \text{salt of } d\text{—acid}/l\text{—base} \\ \text{salt of } l\text{—acid}/l\text{—base} \end{cases}$$

$$dl\text{—base} + l\text{—acid} \rightarrow \begin{cases} \text{salt of } d\text{—base}/l\text{—acid} \\ \text{salt of } l\text{—base}/l\text{—acid} \end{cases}$$

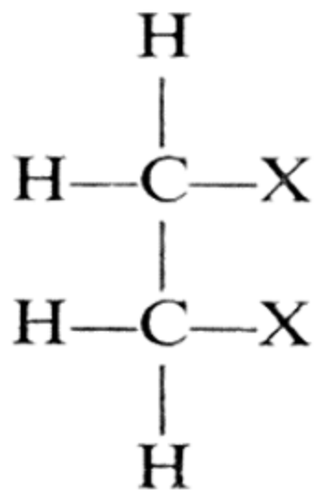
Since these salts are not enantiomorphous, they will have slightly different physical properties, and may be separated, for example, by fractional crystallization. Thus racemic acid may be resolved by neutralizing it with *l*—cinchonidine. *l*—Cinchonidine *d*—tartrate separates first from the aqueous solution. The optically active acids are then recovered from the two salts (after purification by recrystallization) by treatment with acids.

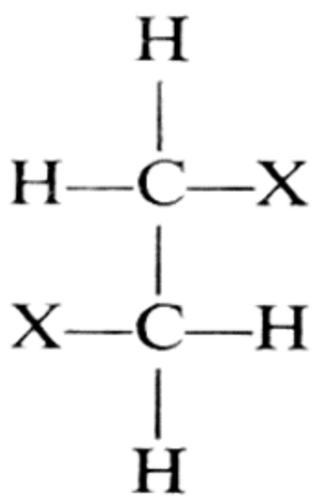
3. *Fermentation Method.* This method, which produces only one of the two active forms, is based on the different physiological activity of the two forms (for example, the dextro-forms of histidine, asparagine, etc., have a sweet taste, whilst the corresponding laevo-forms are practically tasteless; the laevo-forms of adrenaline, nicotine, etc., are more poisonous than the dextro-forms, and so on). The method depends on the fact that if certain living organisms, such as bacteria, yeast or moulds (e.g. pencillium glaucum) are allowed to grow in a solution of a *dl*—mixture, they feed preferentially on one of the two active forms (usually the form which occurs in nature), so that the other may ultimately be recovered.

In conclusion, it should be noted that ordinary synthetic methods produce inactive compounds or mixtures (racemates, meso-compounds, etc.), whilst living processes usually produce one or other of the active forms. Thus grapes produce *d*—tartaric acid and *d*—potassium hydrogen tartrate.

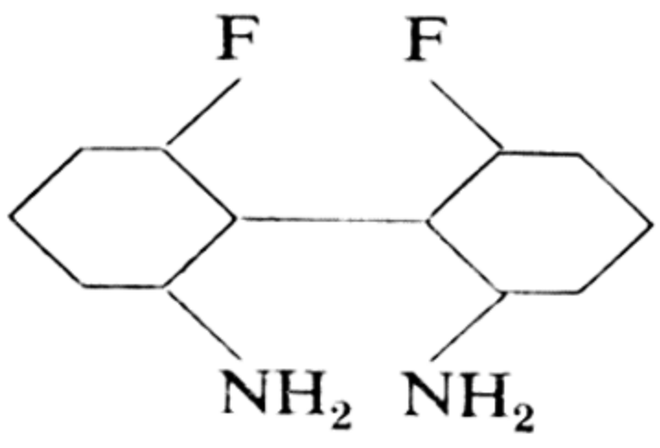
Geometrical or Fixed-space Isomerism

When two carbon atoms are united by a double-bond, the molecule loses its ability to rotate about the carbon-carbon axis, a freedom to rotate which is found, for example, in compounds containing a single carbon-carbon bond. That the latter compounds must possess a relative freedom of rotation about the carbon-carbon bond is evident from the absence of two different compounds having the structures—

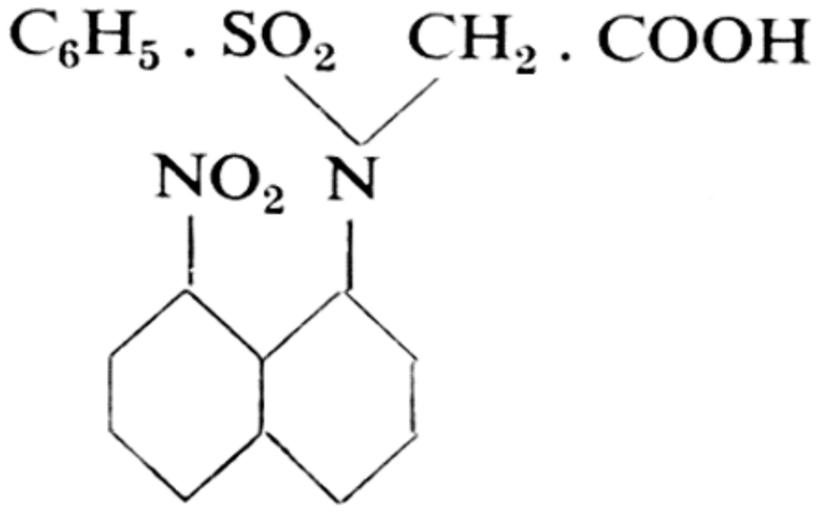




Only one compound, $C_2H_4Cl_2$, for example, is known. It should be added, however, that compounds are known in which this freedom of rotation about a carbon-carbon single-bond is restricted by the size of the substituent groups. This effect is known as *steric hindrance* and may lead to the existence of optically active compounds which do not possess asymmetric carbon atoms, provided the compound does not possess either a plane or centre of symmetry. Examples include—

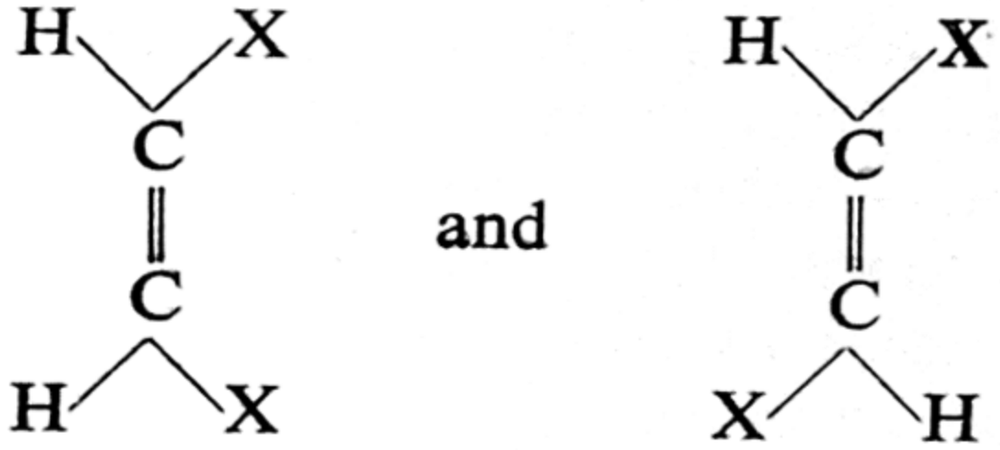


and

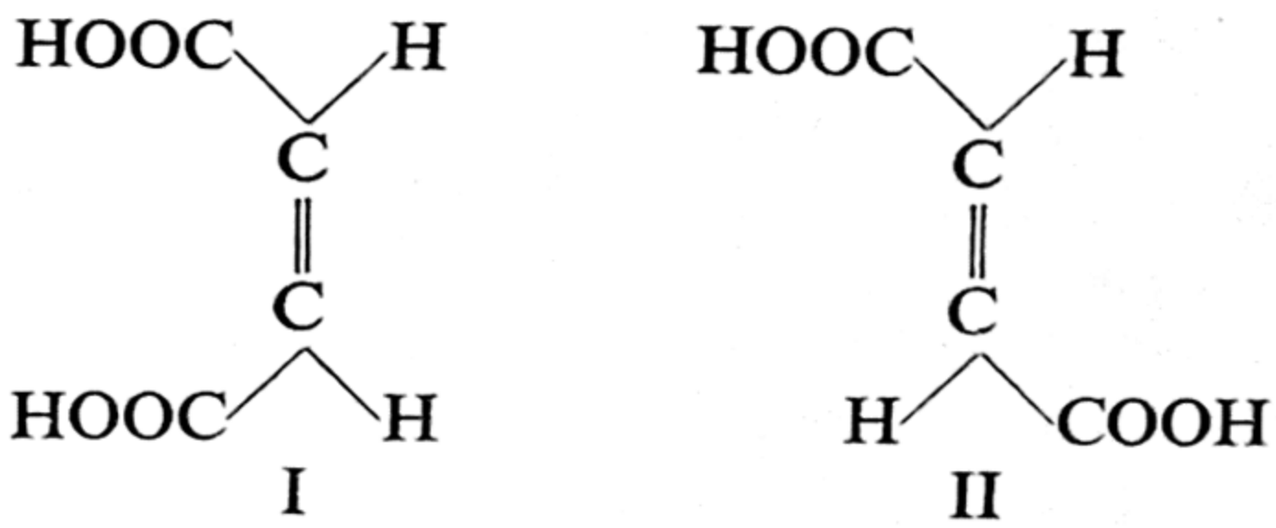


Note. The space-formulae of these compounds do not possess either a centre or plane of symmetry and the compounds therefore are optically active.

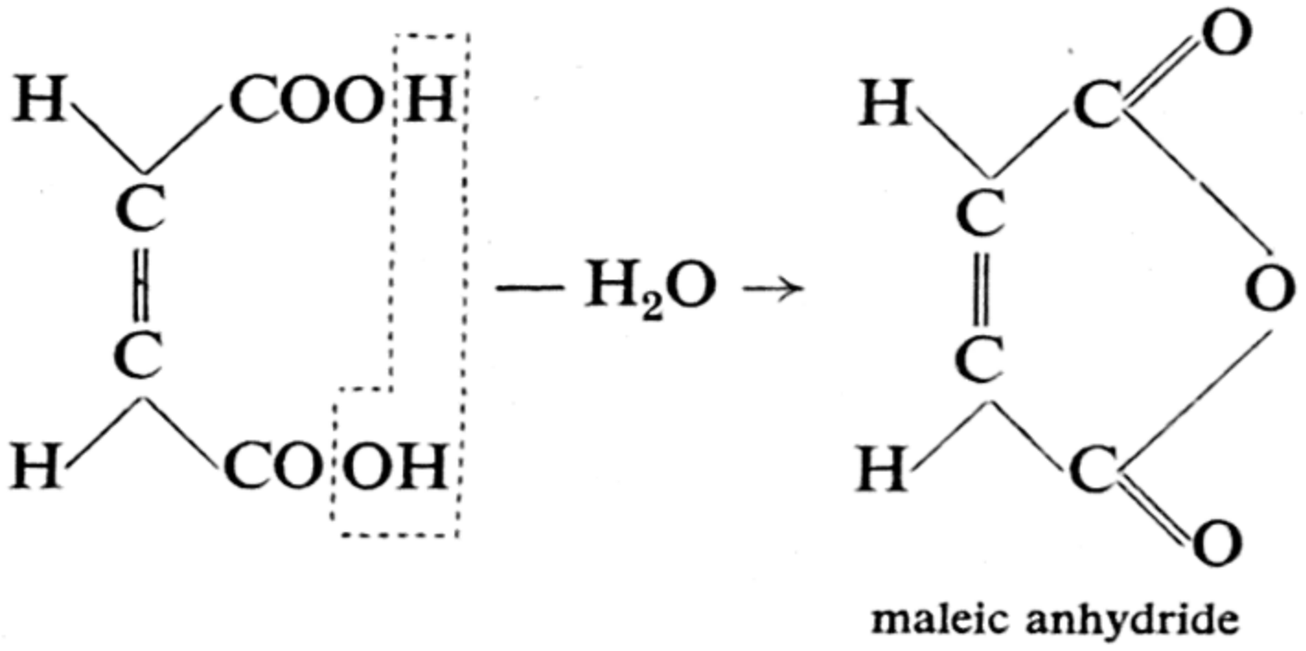
When the two carbon atoms are united by a double-bond, the molecule, so to speak, becomes rigid. It loses its freedom of rotation about the carbon-carbon bond, so that two geometrical isomers should exist having the formulae—



Fumaric and Maleic Acids are examples of this type of geometrical isomerism—



These two acids are *not* optically active (since they each possess a plane or centre of symmetry), and they have quite different chemical and physical properties. Thus, one of the two acids easily forms an anhydride. This is maleic acid and presumably has structure I since in this form the closer proximity of the —COOH groups would appear to facilitate the removal of a molecule of water—

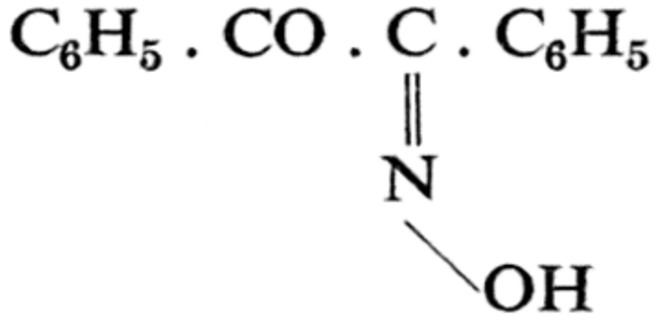


Formula II would then be that of *fumaric* acid.

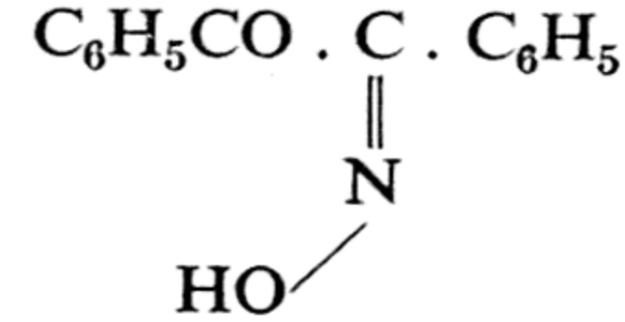
This geometrical or fixed-space isomerism is often referred to as *cis-trans isomerism*. The *cis* form is taken as the form in which similar groups are on the same side of the double bond, and the *trans* form as the one in which the similar groups are on opposite sides of the double bond. When the compounds do not lend themselves to this *cis-* and *trans-* nomenclature,

the distinguishing prefixes α and β are used to differentiate between the geometrical isomers. Examples include not only compounds containing a carbon-carbon double bond, but also compounds containing carbon-nitrogen double bonds, nitrogen-nitrogen double bonds, etc.

Benzil monoxime

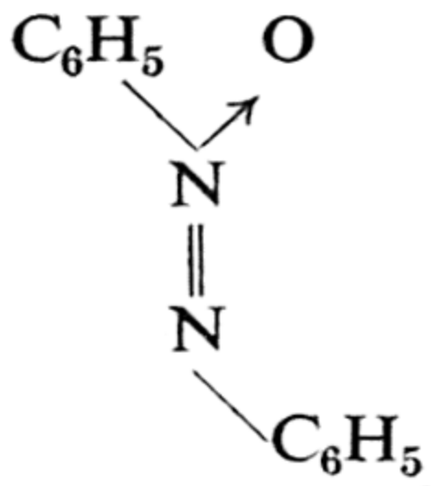


(α-form, m.p. 140°C)

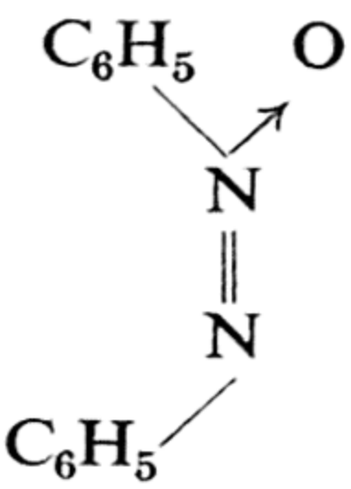


(β-form, m.p. 113°C)

Azoxy-benzene

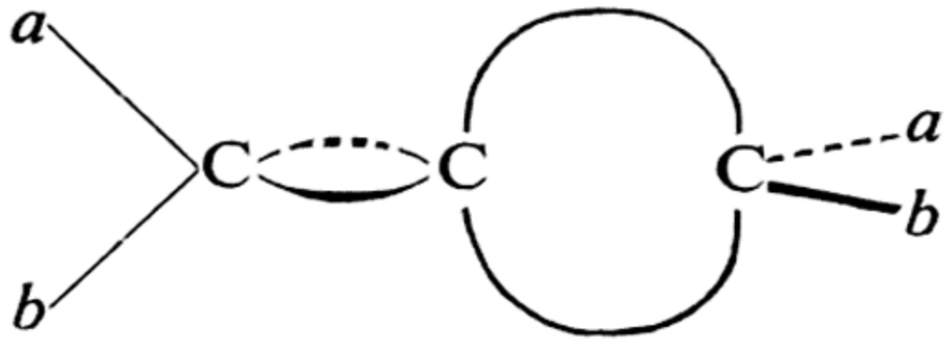


(m.p. 36°C)

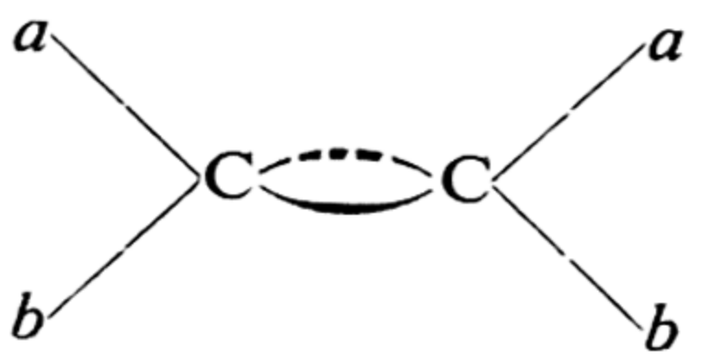


(m.p. 84°C)

In conclusion, it may be stated that compounds containing more than one double bond may be optically active although they do not contain an asymmetric carbon atom. The necessary conditions for optical activity in each case are the absence of (*a*) a plane of symmetry, (*b*) a centre of symmetry and (*c*) an alternating axis of symmetry. These three conditions apply to all cases of optical activity.

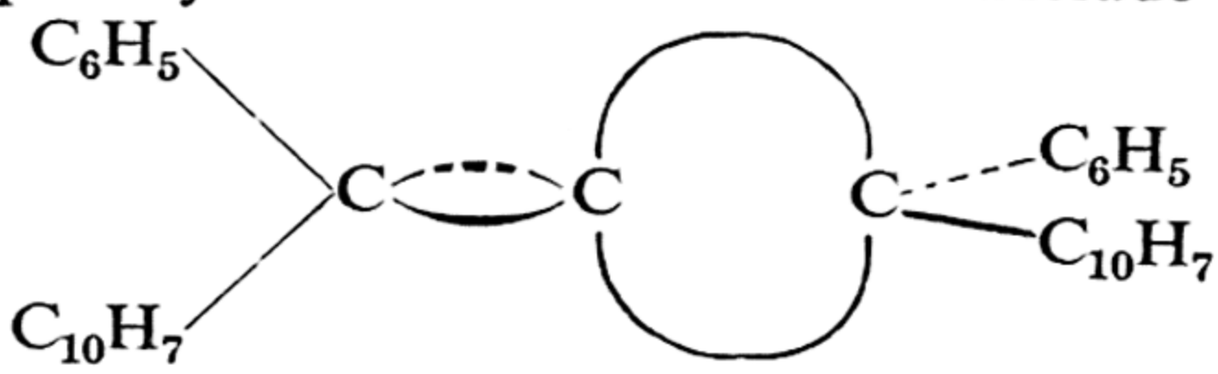


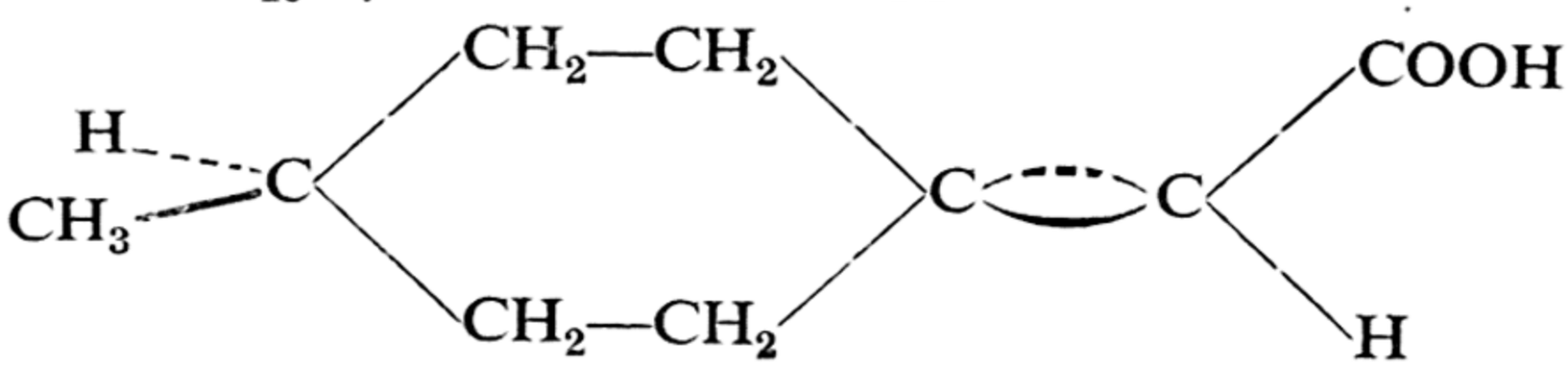
allene derivatives—optically active



ethylene derivatives—geometrical isomerism only

Examples of optically active allene derivatives include—





Note. Neither of these compounds contains an asymmetric carbon atom.

CHAPTER 35

AROMATIC HYDROCARBONS

THE division of organic chemistry into *aliphatic* and *aromatic* had its origin in the characteristic, usually agreable, smell possessed by certain organic compounds. These latter were termed aromatic to distinguish them from the other large class of compound, known as aliphatic, which had somewhat different chemical properties and were related to, or derived from, natural fats. It is now realized that many aromatic compounds are related to benzene, a hydrocarbon with the molecular formula, C_6H_6. The term *aromatic* has in fact nowadays become synonymous with benzene, its homologues and their derivatives.

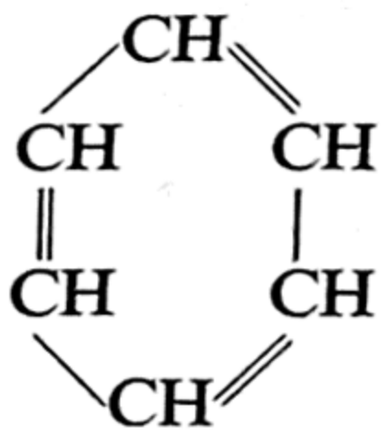
Benzene. The structural formula of benzene, the parent of aromatic organic chemistry, was for a long time an enigma to chemists. Its properties preclude such open-chain formulae as—

$$HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH, \quad CH_3{-}C{=}C{-}C{=}C{-}CH_3$$

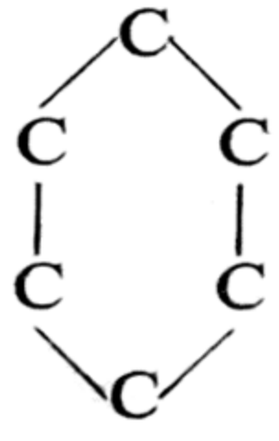
or

$$CH_2{=}C{=}CH{-}CH{=}C{=}CH_2$$

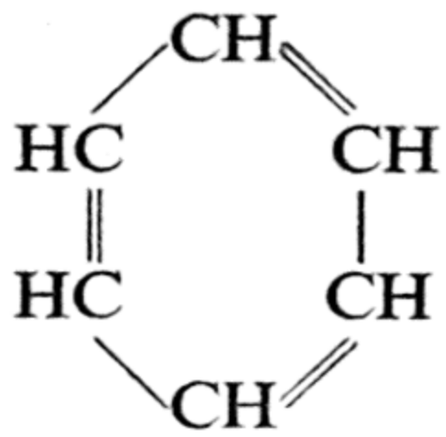
and ring structures such as

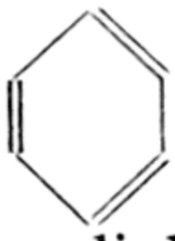
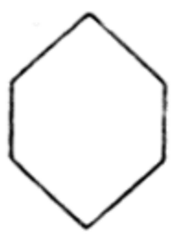


also have certain serious defects. Thus benzene lacks the ease of formation of addition compounds, a property, so characteristic of straight-chain unsaturated compounds, such as ethylene and propylene. These different formulae for benzene are discussed later in the present chapter however, so that for the moment all that need be stated is that the structural formula of benzene is based on a regular six-membered ring of carbon atoms, thus—



and that in its reactions it appears to behave as if it had the regular hexagonal structure



in which the usual unsaturated properties associated with the double bond appear to be more or less masked. This structural formula is usually represented either by  or, more simply, by  in which the hexagon is conveniently drawn slightly elongated.

Preparation. Benzene and certain other aromatic hydrocarbons (toluene, naphthalene, etc.) are obtained industrially from coal-tar, produced as described in Chapter 22 by the destructive distillation of coal. The crude tar is first treated to remove most of the water, and then separated by distillation into the following fractions.

B.P. Range (°C)	Name	Principal Ingredients
Up to 170	Light oil or *Naphtha*	Benzene, toluene, xylene
170–230	Middle oil (or Carbolic oil)	Phenol, naphthalene
230–270	Heavy oil (or *Creosote*)	Cresols, etc.
270–360	Anthracene oil	Anthracene

NOTE: Residue in retort—Pitch

The light oil fraction is redistilled and the fraction boiling between 70°C and 150°C separated. This is then refined by agitating with cold concentrated sulphuric acid to remove basic substances, such as pyridine, ammonia and traces of aniline. The upper benzole layer is separated from the heavier sulphuric acid layer, washed with water and then treated with sodium hydroxide solution to remove carbolic acid (phenol). After further washing and drying, the refined benzole is then redistilled. A typical refined motor-benzole may contain about 70 per cent benzene, 18 per cent toluene and 6 per cent xylenes. These latter compounds may be separated by fractional distillation, based on their different boiling points, benzene 80°C, toluene 110°C and the three isomeric xylenes 138°–142°C. The fraction boiling between 150° and 170°C is sold as an industrial solvent under the name "solvent naphtha." It is used as an illuminant, rubber

solvent and paint thinner, and should not be confused with white-spirit, which is a petroleum distillate.

The benzene obtained in this way from coal-tar contains a small quantity of thiophene, C_4H_4S, a compound which resembles benzene so closely that it cannot be separated by distillation methods. Thiophene, however, is more readily sulphonated than is benzene, and may therefore be removed from the latter by repeatedly shaking with small quantities of concentrated (not fuming) sulphuric acid in the cold. Very pure benzene may then be obtained by cooling in an ice-bath until about 90 per cent of the benzene has crystallized out, and then separating these crystals of pure benzene from the mother liquor.

Benzene may be prepared chemically by such reactions as—

1. Heat benzoic acid (or calcium benzoate) with lime and collect the benzene distillate—

$$C_6H_5 . COOH + CaO \rightarrow C_6H_6 + CaCO_3$$

This reaction recalls the method for producing methane by heating sodium acetate with soda-lime.

2. Since any benzene hydrocarbon (e.g. toluene) is converted into benzoic acid on oxidation, and the latter on distillation with lime produces benzene, it follows that benzene may easily be obtained from any of its homologues—

$$\underset{\text{toluene}}{C_6H_5 . CH_3} \xrightarrow{\bar{O}} C_6H_5 . COOH \xrightarrow{CaO} C_6H_6$$

3. Small quantities of benzene may also be obtained by passing acetylene through a tube heated to a dull red heat—

$$3C_2H_2 \text{ (polymerization)} \rightarrow C_6H_6$$

Properties. Benzene is a colourless mobile liquid with a characteristic odour. It boils at 80·5°C and when pure freezes at 5·4°C. It is less dense than water (0·87, cf. 1) with which it is immiscible, but mixes readily with most organic solvents (alcohol, ether, etc.) and is a good solvent for most organic compounds (fats, waxes, resins, rubber, etc.) sulphur and iodine. Like acetylene, benzene burns with a luminous smoky flame, due to the relatively high percentage of carbon, and is used as a liquid fuel, for example in motor benzole. It is also used in dry cleaning and as the parent compound in the synthesis of other aromatic compounds among which may be mentioned dye-stuffs, drugs and antiseptics.

In spite of its apparently highly unsaturated nature, benzene is characterized by a remarkable chemical degree of stability. The six-membered ring of carbon atoms present in benzene and its homologues remains intact throughout many of the numerous reactions which these compounds undergo. Benzene, for example is unaffected by ordinary oxidizing or reducing agents, by dilute acids or boiling aqueous alkalis, and does not

decolorize bromine water. It is only very slowly oxidized by hot acidified permanganate to form oxalic and formic acids, and is only reduced with difficulty to cyclohexane by passing benzene vapour and hydrogen repeatedly over a finely divided nickel catalyst at about 200°C—

$$C_6H_6 + 3H_2 \rightarrow \underset{\text{cyclo-hexane}}{C_6H_{12}}$$

Under certain conditions, benzene will also form addition compounds with chlorine and bromine. Reaction occurs in the vapour phase in the presence of bright sunlight to form hexachloro- and hexabromo-benzene.

$$C_6H_6 + 3Cl_2 \rightarrow C_6H_6Cl_6$$

Addition also occurs with ozone to form the tri-ozonide, $C_6H_6O_9$. The fact that in all these addition reactions the maximum number of univalent groups (or atoms) added is six and no more should be noted, since, as discussed later, it affords evidence for the Kekulé formula of benzene with its alternate single and double bonds.

The stability of the benzene ring is even more strikingly revealed by the following substitution reactions which are characteristic of benzene and its homologues—

Nitration

$$C_6H_6 + HNO_3 \rightarrow \underset{\text{nitro-benzene}}{C_6H_5 \,.\, NO_2}$$

When benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid, one of the hydrogen atoms of the benzene is substituted by the univalent nitro-group (—NO_2) to form nitro-benzene, which is a pale yellow oil. The function of the concentrated sulphuric acid appears to be to remove the water which forms during the substitution—

$$C_6H_5 \,.\, \boxed{H + HO}\text{–}NO_2 \rightarrow C_6H_5 \,.\, NO_2 + H_2O$$

but see also below.

Further substitution may occur under more powerful conditions to form dinitro-benzene, $C_6H_4(NO_2)_2$, in which two hydrogen atoms of the benzene molecule are replaced by nitro groups. Note, that paraffins, except tertiary paraffins, such as $(CH_3)_3CH$, do not react with concentrated nitric acid.

Sulphonation

$$C_6H_5 \,.\, \boxed{H + HO} \,.\, SO_2 \,.\, OH \rightarrow C_6H_5 \,.\, SO_2OH + H_2O$$

When benzene is heated with concentrated sulphuric acid, substitution occurs to form benzene sulphonic acid, $C_6H_5 \,.\, SO_2OH$. Further substitution to form benzene di-sulphonic acid occurs with fuming sulphuric

acid. Benzene sulphonic acid is a colourless deliquescent solid, readily soluble in water (note this action of concentrated sulphuric acid in converting an insoluble hydrocarbon into a water soluble sulphonic acid), and is a strong monobasic acid.

Halogenation

$$C_6H_5 . H + Br-Br \rightarrow C_6H_5Br + HBr$$

Substitution of one of the benzene hydrogen atoms for chlorine or bromine occurs at relatively low temperatures in the presence of a suitable catalyst, such as iron filings, aluminium or iodine. Thus reaction between bromine and benzene occurs at ordinary temperatures in the presence of iron, pyridine, etc. (but in the absence of direct sunlight) to form bromobenzene, C_6H_5Br, and a small quantity of para-dibromobenzene. In the presence of direct sunlight, addition reactions occur, particularly in the hot, to form benzene hexabromide, $C_6H_6Br_6$. Chlorobenzene and bromobenzene are heavy insoluble oils, and unlike the alkyl halides are not very reactive. Thus, they are mostly unaffected by alkalis, alcoholic ammonia, potassium cyanide, etc. They do, however, take part in the Fitting reaction (*see* below), and also form Grignard reagents with magnesium.

Friedel and Craft's Reaction. When benzene is treated with an alkyl or acyl chloride, in the presence of finely-powdered anhydrous aluminium chloride as catalyst, the following substitution reactions occur—

$$C_6H_5 . H + Cl . CH_3 \rightarrow C_6H_5 . CH_3$$

alkyl chloride — toluene

$$C_6H_5 . H + Cl . CO . CH_3 \rightarrow C_6H_5 . CO . CH_3$$

acetyl chloride — aceto-phenone or phenyl methyl ketone

This reaction, which is a useful one for preparing homologues of benzene, does not occur with aliphatic hydrocarbons and is thus characteristic of aromatic compounds.

Differences between Aliphatic and Aromatic Hydrocarbons

Aromatic hydrocarbons readily undergo substitution reactions with concentrated nitric and sulphuric acids at quite moderate temperatures. Aliphatic hydrocarbons in general do not react with these acids.

Aromatic hydrocarbons undergo the Friedel and Craft reaction; aliphatic hydrocarbons do not.

Aliphatic halides are very reactive; the aromatic halides in which the halogen is directly linked to the benzene ring, as in bromobenzene, are comparatively inert.

Whereas benzene is almost inert to oxidizing agents, its homologues,

such as $C_6H_5.CH_3$, $C_6H_5.CH_2.CH_3$, etc. are easily oxidized to benzoic acid, or similar compounds.

$$C_6H_5 . CH_3 \rightarrow C_6H_5 . COOH$$

benzoic acid

$$(C_6H_5)_2CH_2 \rightarrow (C_6H_5)_2CO$$

di-phenyl ketone

Aliphatic hydrocarbons, on the other hand, resist oxidizing agents.

Compounds containing the phenyl group (C_6H_5—) are appreciably more acidic than the corresponding purely aliphatic compounds. The phenyl group, in fact, tends to impart an acidic character to the molecule, whilst the methyl group tends to impart a basic character. Thus—

Phenol, C_6H_5OH, acidic, and not esterified by acetic acid;
Methyl alcohol, CH_3OH, neutral, but forms methyl acetate.

CH_3NH_2, more basic than NH_3 which is more basic than $C_6H_5NH_2$.

$C_6H_5.COOH$, strong acid; $CH_3.COOH$, very weak acid.

Aromatic primary amines, e.g. aniline ($C_6H_5 . NH_2$), form the very important *diazo-compounds* with nitrous acid. Aliphatic primary amines do not give diazo-compounds. Both, however, ultimately liberate nitrogen to form the hydroxy-compound, although with the aromatic primary amines, this further reaction only occurs on warming.

Reduction of nitro-compounds leads in both aromatic and aliphatic compounds to the formation of amines, but in the case of aromatic nitro-compounds, a number of intermediate reduction products may be isolated—

$$C_6H_5NO_2 \rightarrow \underset{\text{nitrosobenzene}}{C_6H_5NO} \rightarrow \underset{\text{phenyl-hydroxylamine}}{C_6H_5NHOH} \rightarrow \underset{\text{aniline}}{C_6H_5 . NH_2}$$

$$\begin{matrix} C_6H_5NO_2 \\ + \\ C_6H_5NO_2 \end{matrix} \rightarrow \underset{\text{azoxybenzene}}{\begin{matrix} C_6H_5NO \\ \| \\ C_6H_5N \end{matrix}} \rightarrow \underset{\text{azobenzene}}{\begin{matrix} C_6H_5N \\ \| \\ C_6H_5N \end{matrix}} \rightarrow \underset{\text{hydrazobenzene}}{\begin{matrix} C_6H_5NH \\ | \\ C_6H_5NH \end{matrix}}$$

Structure of Benzene

It has already been stated in the introduction to the present chapter that the structural formula of benzene was for a long time a thorn in the sides of organic chemists. Its molecular formula was soon shown by the usual methods to be C_6H_6, and at first various linear formulae, such as

$$HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH, \quad CH_3{-}C{\equiv}C{-}C{\equiv}C{-}CH_3$$

and

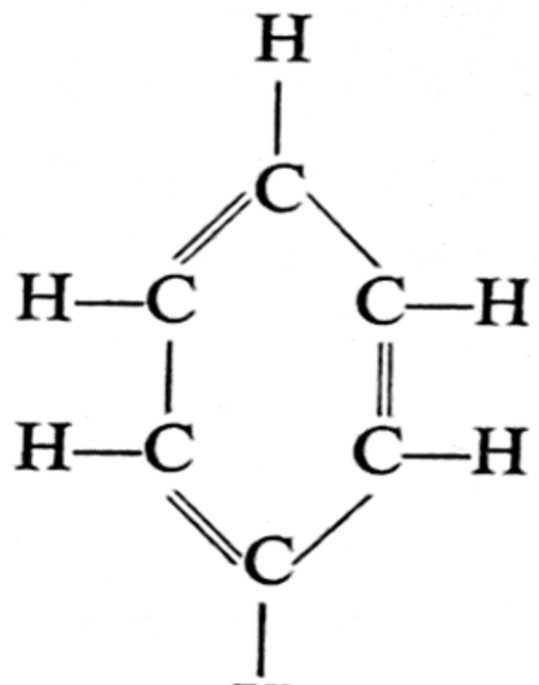
$$CH_2{=}C{=}CH{-}CH{=}C{=}CH_2$$

were suggested, but these were soon ruled out in the face of the following facts—

(*a*) All the six hydrogen atoms of benzene are equivalent. In other words, there are no isomers but only *one* compound with the formula C_6H_5X. This fact rules out the first and third of the above formulae, but not the second.

(*b*) Although benzene does not normally undergo addition reactions, this fact is of less importance than the observation that when it does so react the maximum of univalent groups which it adds on is not eight, as would be required by the above formulae, but six.

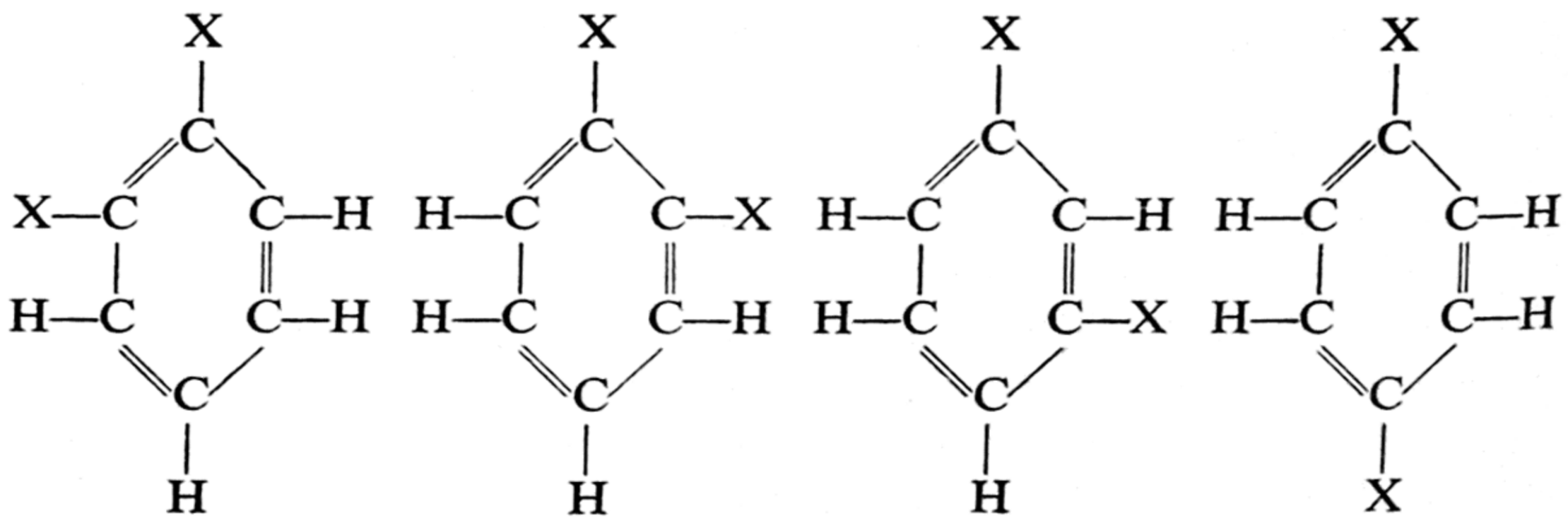
In 1867, Kekulé put forward his celebrated ring formula in which the six carbon atoms are alternately linked by single and by double bonds.



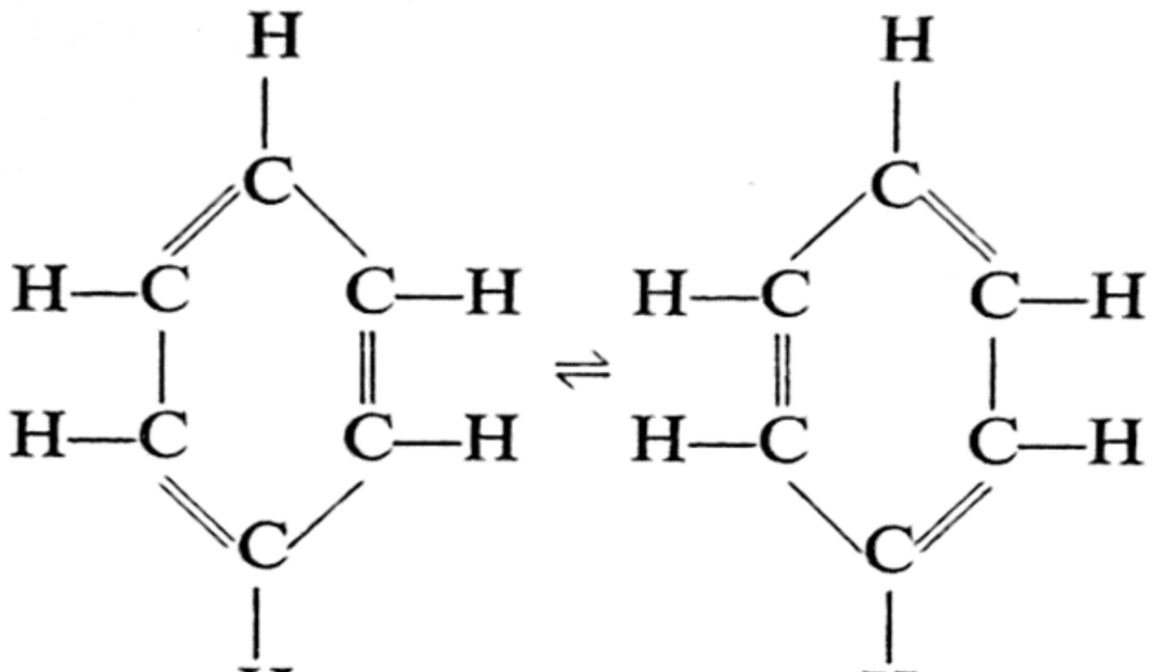
This formula satisfactorily explained the equivalence of the six hydrogen atoms, but suffered from the following disadvantages—

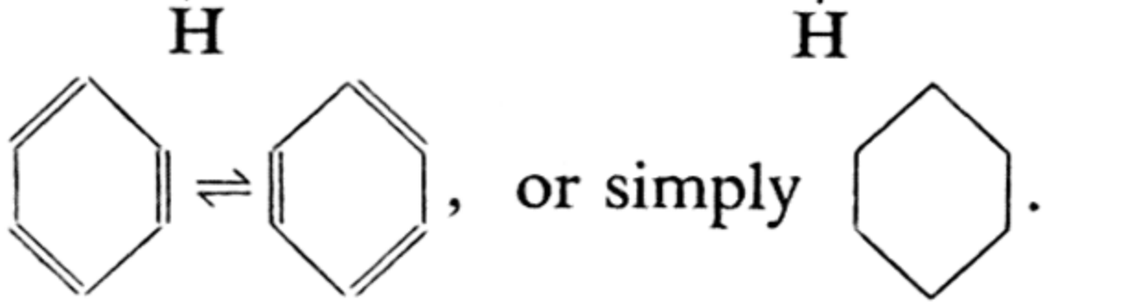
(*a*) Its resemblance to olefine compounds does not explain the fact that benzene only forms addition compounds under certain special conditions.

(*b*) Such a structural formula would permit of four isomers with the formula $C_6H_4X_2$, whereas only three such isomers are in fact known. These four isomers would be represented by the following formulae—



To meet this latter objection, Kekulé in 1872 put forward his "dynamic" formula in which the double bonds are regarded as oscillating between the two extreme forms—

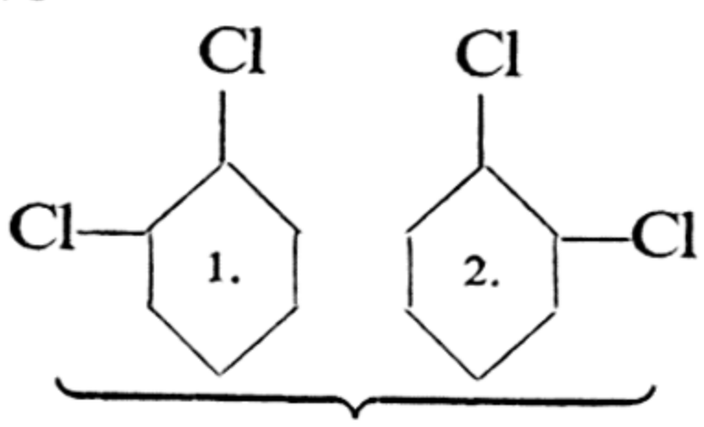




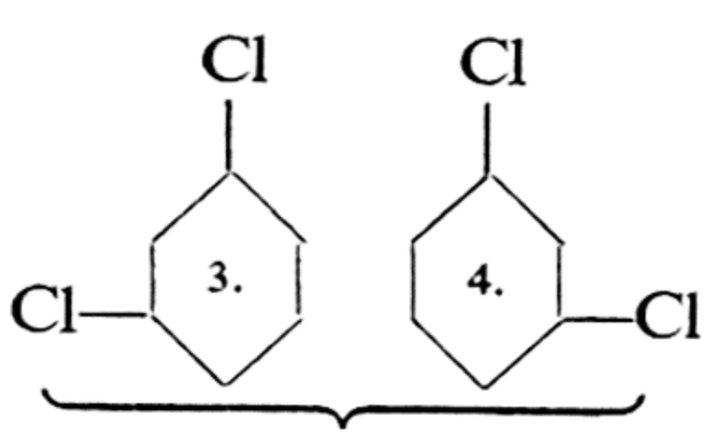
or conventionally, , or simply .

With this dynamic formula, the first two of the above di-substitution formulae become identical, and the total number of different di-substitution compounds is reduced to three, in agreement with fact.

In studying the above formulae, it should be noted that although the six hydrogen atoms in benzene are equivalent, they are no longer all equivalent once one of the hydrogens has been replaced by a substituent group or atom (such as —Cl, —Br, —NO_2, —SO_2OH, etc.). In fact, three different isomeric disubstitution compounds become possible, as described above—



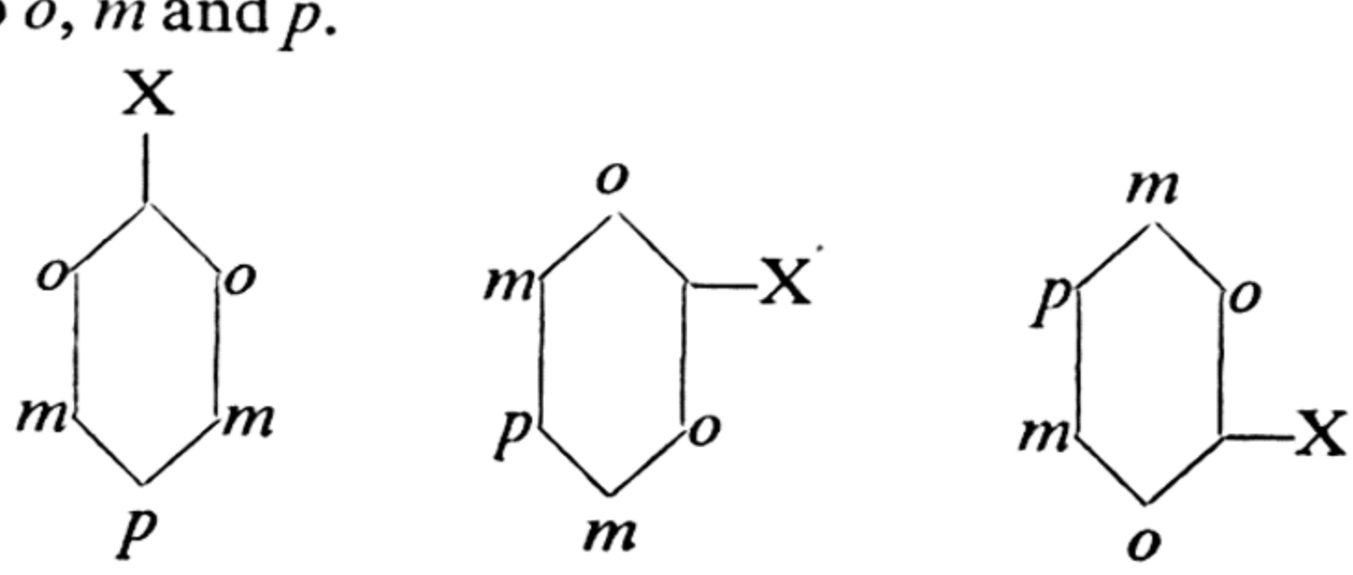
ortho-dichlorobenzene



meta-dichlorobenzene

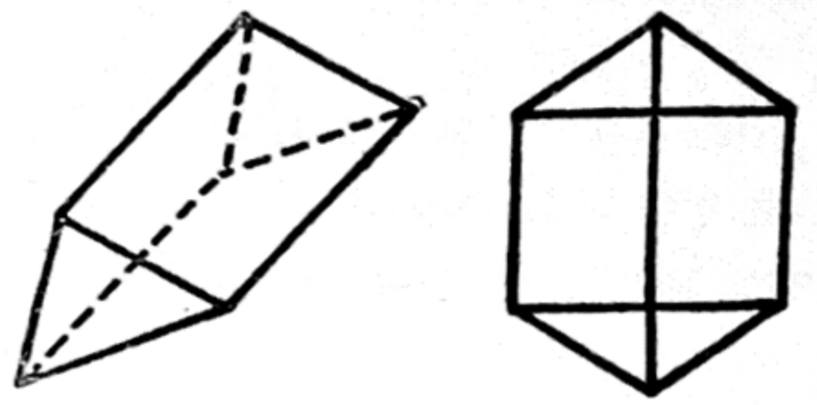
para-dichlorobenzene

Formulae 1 and 2 are of course identical on Kekulé's dynamic formula, as also are formulae 3 and 4. It is conventional to call compounds in which the second substituent enters on either carbon adjacent to that containing the first substituent as *ortho*, on the middle carbon atoms as *meta*, and on the farthest carbon atom as *para*. These prefixes are often abbreviated to *o*, *m* and *p*.

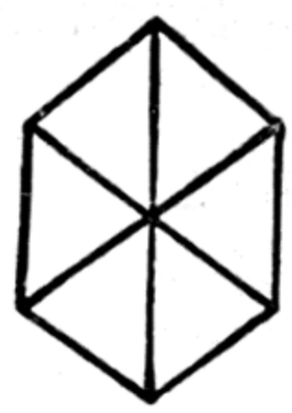


Numerous modifications of the Kekulé ring formula for benzene were proposed at various times in an effort to account for its reluctance to form addition compounds. Limitations of space, however, permit only of the following brief description of these formulae—

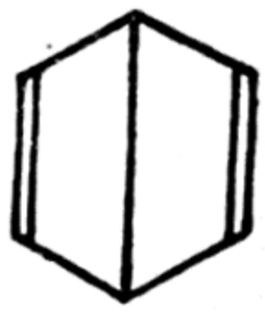
(*a*) *Ladenburg's Prism Formula.* Each carbon atom is considered to be linked by single bonds to three other carbon atoms. The obvious drawback of this formula is that it would be very difficult to account for any of the addition compounds of benzene.



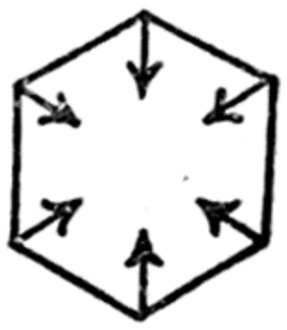
(*b*) *Claus's Formula.* This formula would explain the reluctance of benzene to form addition compounds, since less energy would presumably be required to break the much longer, and therefore weaker, central linkages. Such a formula, however, suggests that benzene might easily form cyclo-butane derivatives.



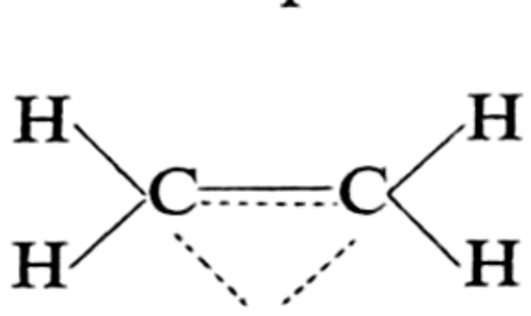
(*c*) *Dewar's Formula.* This formula suffers from the same difficulty as the previous formula, in that it again suggests that benzene should readily form cyclo-butane derivatives.

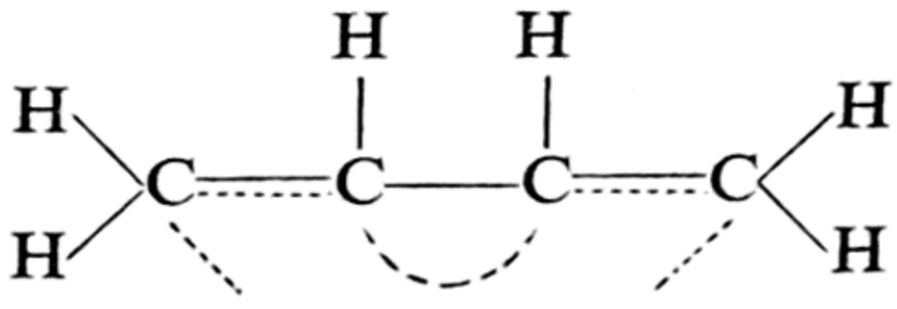


(*d*) *Armstrong-Baeyer Centric Formula.* In this formula, the fourth carbon valency bond is considered to be directed towards the centre of the ring. Such a formula is very indefinite, and the latent fourth valency which it implies appears merely to beg the question.



(*e*) *Thiele's "Partial-valency" Formula.* Thiele was led to this formula from a study of the addition reactions of compounds containing conjugated double bonds, that is, alternate single and double bonds, as in $CH_2=CH—CH=CH_2$. With HBr this latter compound forms an addition compound, $CH_2Br—CH=CH—CH_3$, the addition occurring on the end carbon atoms. This led Thiele to suggest that the formation of a double bond only partially neutralizes the valency bonds, and that addition occurs as a result of the partial free valencies—

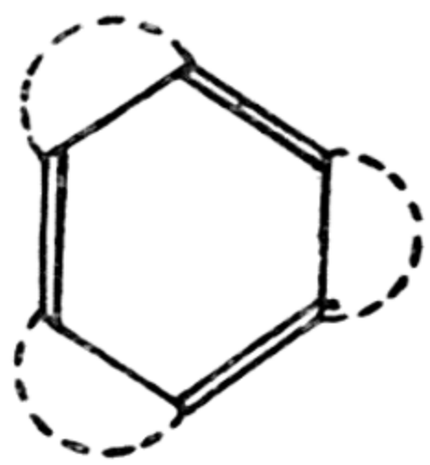




In the latter compound, butadiene, the partial free valencies on the two middle carbon atoms mutually saturate each other, and only the two end carbon atoms retain their partial free valencies. Such a theory would

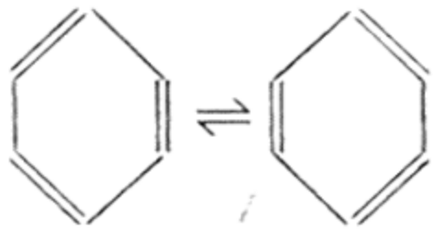
explain the tendency of butadiene in addition reactions to add on only at the two *end* carbon atoms.

Applied to benzene, Thiele's theory suggests the formula—



Since there is no marked unsaturation, such a formula as this would explain the reluctance, but would not preclude, the formation of addition comopunds with benzene. It should be noted, however, that this formula suffers from the same difficulty as the Kekulé static formula as regards the possible number of di- and tri-substitution derivatives.

Present-day Views. The dynamic formula of Kekulé is considered to be remarkably close to the truth. Instead, however, of postulating a *tautomeric* change between two extreme formulae, namely—



it is suggested, on the *resonance theory*, that benzene has some intermediate structure, which cannot simply be depicted by any one structural formula. We speak of benzene as a *resonance hybrid* of the two Kekulé formulae. The effects of this resonance are—

(*a*) To give the benzene ring a regular planar hexagonal structure, as required by X-ray crystal structure analysis. Neither of the Kekulé formulae would be truly hexagonal, since a double-bond is somewhat shorter than a single bond (1·34, cf. 1·54 Å units).

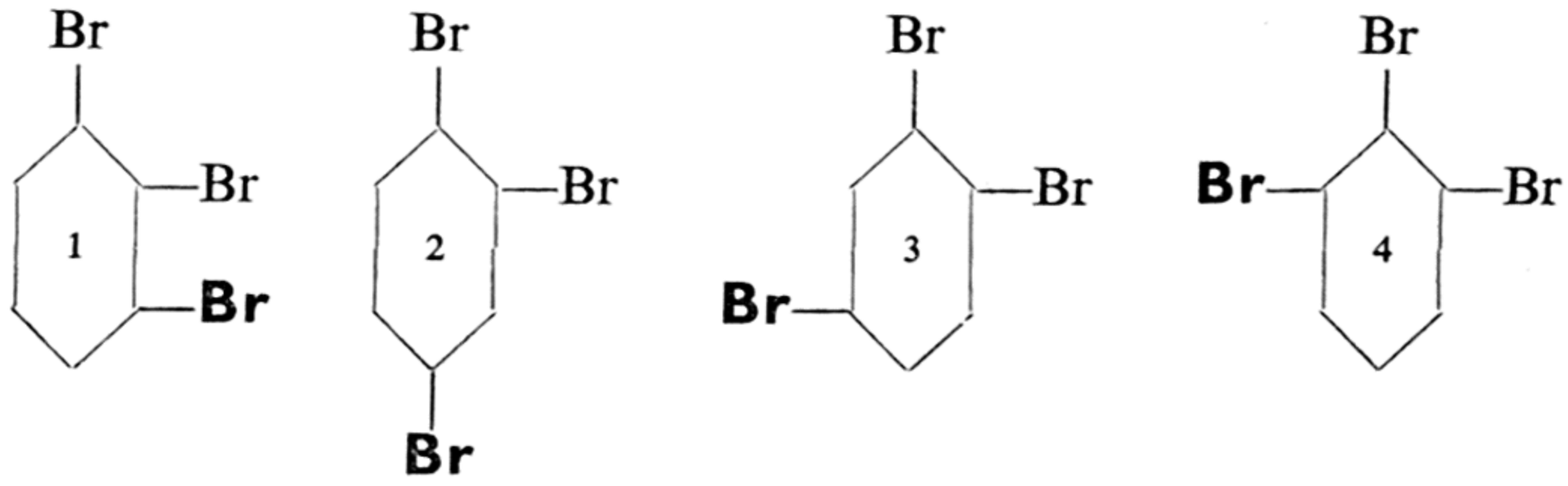
(*b*) To reduce the energy content to a value below that possessed by a hypothetical compound having either of the Kekulé formulae. Reduction in energy leads to increased stability and this increased stability, which is conferred on benzene by resonance, is sufficient to account for its reluctance to form addition compounds. When benzene undergoes addition reactions, the energy of the reaction must be sufficient to overcome this resonance energy and bias the molecule to one or other of the Kekulé formulae. The normal addition reactions associated with the presence of one or more double bonds may then occur.

To recapitulate, in the normal state benzene is a resonance hybrid of the two Kekulé structures, that is, something with a lower energy content than either of these two structures and not just a physical mixture. Before it can react, sufficient energy has to be supplied (by heating) to overcome the resonance energy and convert it into one or other of the Kekulé structures. In this form benzene can then undergo the usual addition and substitution reactions. When one substituent is already present in the molecule, the resonance state of the molecule is modified in the direction of one or other of the two Kekulé formulae, and further substitution occurs either in the ortho and para positions or in the meta positions depending on

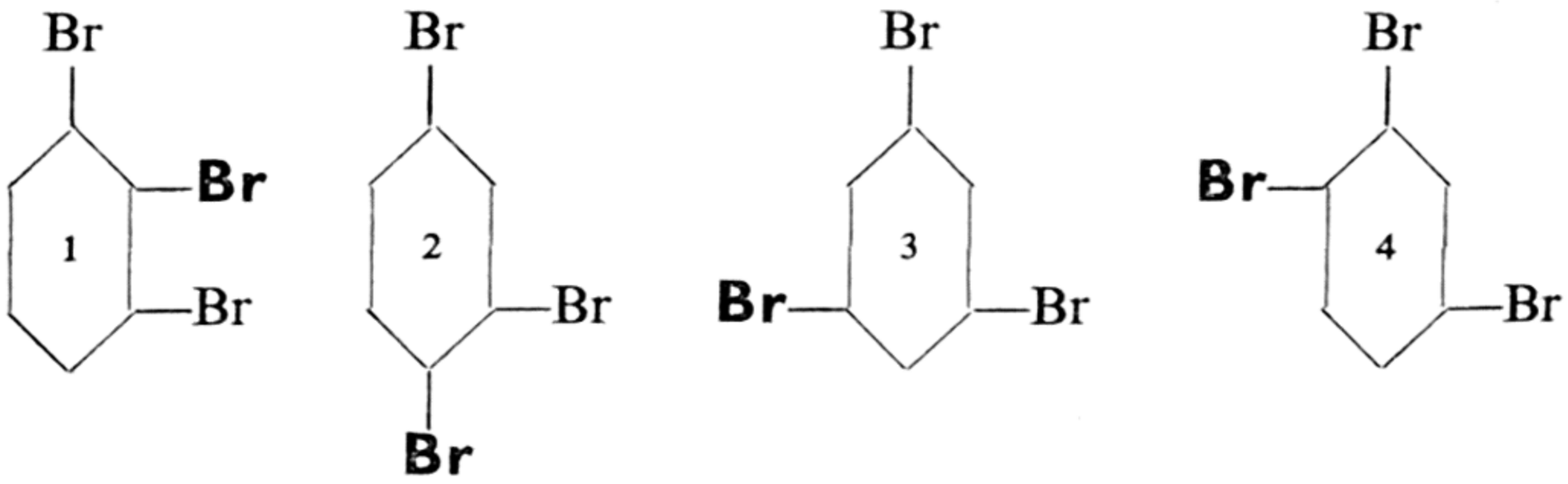
the nature of the substituent. A fuller discussion of the effect of a substituent in determining at which carbon a second substituent will enter is given in the following section.

Orientation in the Benzene Nucleus. The problem of determining the relative position of substituents in the benzene nucleus is known as *orientation*. Korner's general method for determining the relative position of the substituents in di-substituted benzene is based on the fact that each of the three possible di-substitution compounds produces a different number of tri-substitution compounds. Thus, three di-bromobenzenes, melting at 7·8°, — 6·5° and 89°C respectively, are known. The problem is to determine which of these is the ortho-, which the meta- and which the para-compound. The procedure is to convert each of these dibromo-benzenes into tribromobenzene, and then determine the number of different tribromobenzenes produced in each case.

Dealing first with the ortho-dibromobenzene, reference to the following formulae shows that only two different tribromobenzenes can be produced. The third formula is identical with the second, and the fourth with the first.

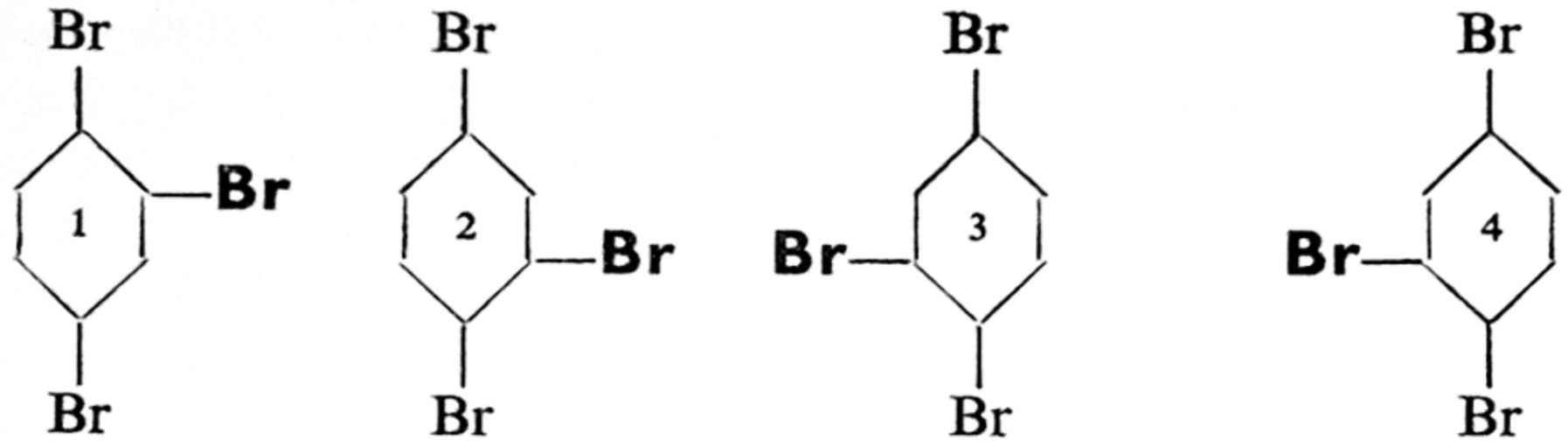


Similarly, the meta-dibromobenzene can form only three different tribromobenzenes, as shown below, the fourth formula being identical with the second.



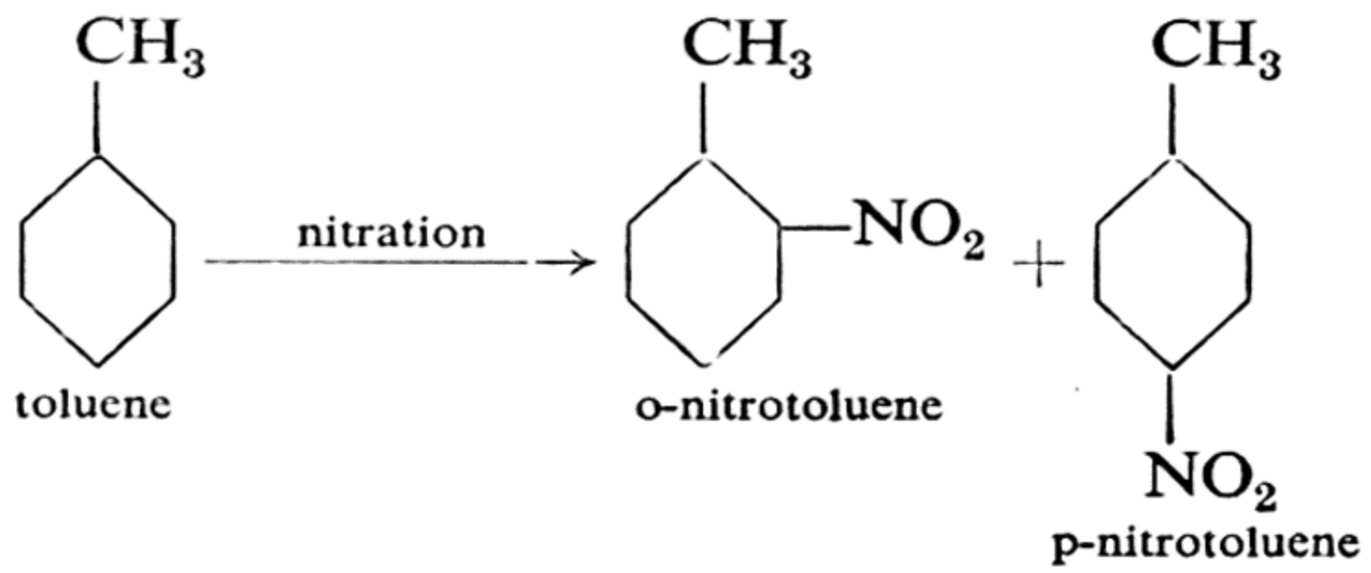
Finally, the para-dibromobenzene can produce only one tri-bromo-benzene, the four formulae (p. 987) being identical.

Thus, the dibromobenzene which produces two tribromo-derivatives must be ortho-dibromobenzene; the one which produces three tribromo-derivatives must be the meta-dibromobenzene; and the one which only forms one tribromo-derivative must be the para-dibromobenzene.

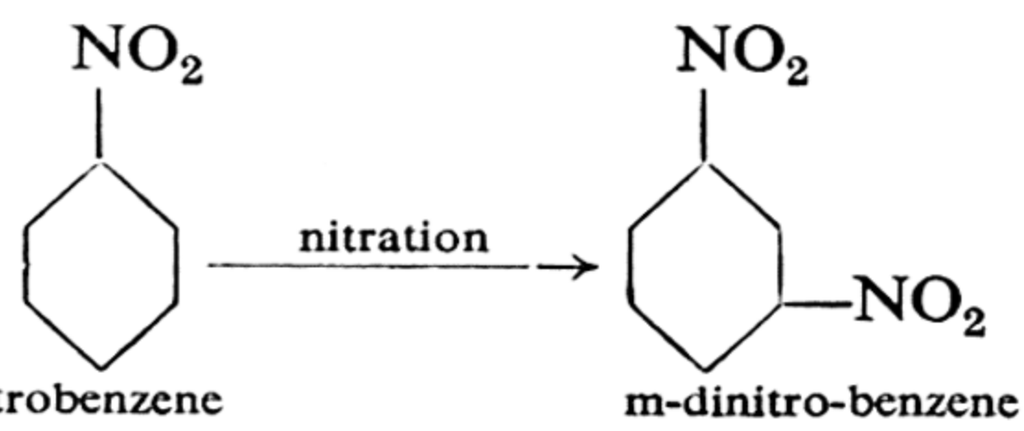


Substitution in the Benzene Nucleus. It has already been stated that substitution in the benzene ring of mono-substituted benzenes is determined by the nature of the substituent already present. Thus toluene, in which the substituent is the CH_3— group, produces a mixture of ortho and para di-substitution compounds when nitrated, chlorinated, brominated, or sulphonated. Nitrobenzene, on the other hand, tends to form meta-di-substituted derivatives and very little of either the ortho- or meta-compounds. The substituents present in the mono-substituted benzenes thus fall into two classes, depending on whether they are ortho and para directing, or meta directing.

The chief *ortho and para directing* groups include —OH, —OCH_3, —NH_2, —Cl, —Br, —I, —CH_3; e.g.—



The chief *meta directing* groups include —NO_2, —COOH, —SO_2OH, —CN, —CHO, —$COCH_3$.



As regards the relative ease of reaction, it should be noted that the ortho-para reactions occur very much more easily than the meta reactions. Thus ortho-para substitution, as exemplified for example by the very ready reaction at ordinary temperatures of aniline or phenol with bromine water, usually takes place under quite mild conditions; meta-substitution, on the other hand, occurs much more slowly and requires much stronger conditions.

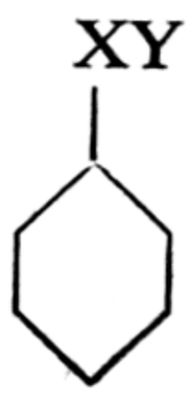
In the following section are described some of the rules which have been

put forward at various times for determining whether a given atom or group is either ortho-para or meta directing. These rules are for the most part only empirical, however, and sometimes give the wrong answer.

Crum Brown's Rule. For a substituent X, if the hydride HX can easily be oxidized to HXO, then X is meta directing. If not, then X is ortho-para directing. Thus, considering nitrobenzene, X is —NO_2, and since HNO_2 can easily be oxidized to HNO_3, it follows that the nitro group is meta-directing. Similarly, for chlorobenzene, since HCl cannot easily be oxidized to HClO, the substituent —Cl should be ortho-para directing.

Vorlander's Rule. If the substituent X contains a double or triple bond, then X will be meta directing. If not, then X is ortho-para directing. Reference to the above classification of ortho-para and meta directing substituents shows the latter obey this rule.

Hammick and Illingworth's Rule. If a monosubstituted benzene derivative has the formula



where X is the atom joined to the benzene ring and Y an atom or group of atoms attached to X, then—

XY is meta directing if—

(*a*) Y is in a higher group in the Periodic Classification than X;
(*b*) Y is in the same group as X, but is of lower atomic weight.

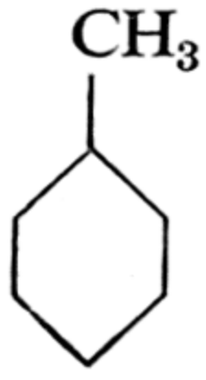
XY is ortho-para directing if—

(*a*) Y is in a lower group than X;
(*b*) X and Y are atoms of the same element;
(*c*) the group XY consists of one atom only.

In applying the latter rule, hydrogen is considered as being in Group I. If, however, Y consists of hydrogen *and* another element (as in —CHO), the hydrogen may be ignored and the rule applied to the second element.

HOMOLOGUES OF BENZENE

Toluene, $C_6H_5 . CH_3$



Toluene is obtained commercially from coal-tar in large quantities, but on a smaller scale it may be obtained by the following methods.

1. *Fittig's Reaction.* This reaction is an extension of the Wurtz synthesis of aliphatic hydrocarbons. A mixture of bromobenzene and an alkyl halide is treated in ethereal solution with finely powdered sodium. Reaction occurs in the cold. The ether is then distilled off and the toluene separated by further distillation.

$$C_6H_5\,Br + 2Na + Br\,CH_3 \rightarrow C_6H_5\,.\,CH_3 + 2NaBr$$

(Finely divided sodium may be prepared by melting sodium under dry benzene followed by well shaking the mixture, but the operation should only be performed by an experienced chemist).

2. *Friedel and Craft's Reaction.* This reaction in which one of the nuclear hydrogen atoms of benzene is substituted by an alkyl group, is carried out by treating a mixture of benzene and the alkyl halide with freshly prepared, finely powdered, anhydrous aluminium chloride.

$$C_6H_5\,.\,H + Cl\,CH_3 \xrightarrow{AlCl_3} C_6H_5\,.\,CH_3 + HCl$$

By this method each of the benzene hydrogen atoms may in turn be replaced by alkyl groups. In practice, to obtain a good yield, excess of aluminium chloride has to be used, usually about one gramme-molecule for each gramme-molecule of the reacting alkyl halide.

3. By distilling toluic acid with lime—

$$CH_3\,.\,C_6H_4\,.\,COOH + CaO \rightarrow CH_3\,.\,C_6H_5 + CaCO_3$$

4. From aromatic organo-magnesium compounds (Grignard Reagents) by heating with alkyl halides, or more conveniently by the action of dimethyl sulphate—

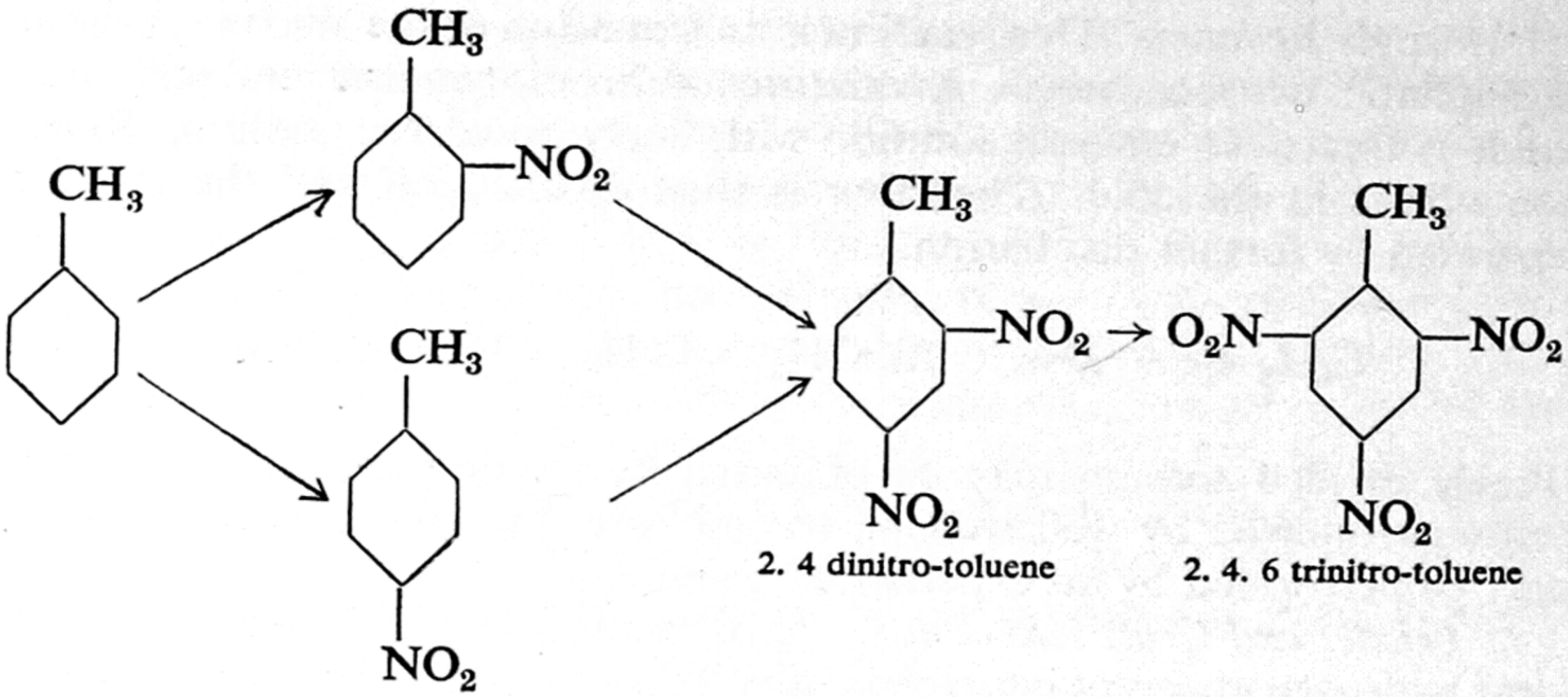
$$C_6H_5\,.\,MgBr + CH_3Br \rightarrow C_6H_5\,.\,CH_3 + MgBr_2$$

5. By heating the corresponding sulphonic acid with steam, in the presence of either sulphuric or hydrochloric acids—

$$CH_3\,.\,C_6H_4\,.\,SO_2OH + H_2O \rightarrow C_6H_5\,.\,CH_3 + H_2SO_4$$

Properties. Toluene resembles benzene in physical properties, and also in its chemical properties, but with certain differences due to the fact that toluene contains both an aromatic and an aliphatic portion. Thus it undergoes the same general reactions, such as nitration, sulphonation, Friedel and Craft's reaction, etc., as benzene, but since the methyl group is ortho-para directing these reactions will in general occur very much more easily with toluene.

Nitration. Toluene is easily nitrated by concentrated nitric acid to give a mixture of ortho- and para-nitrotoluene. Further nitration gives the same 2 . 4 dinitro-toluene, and ultimately trinitro-toluene.



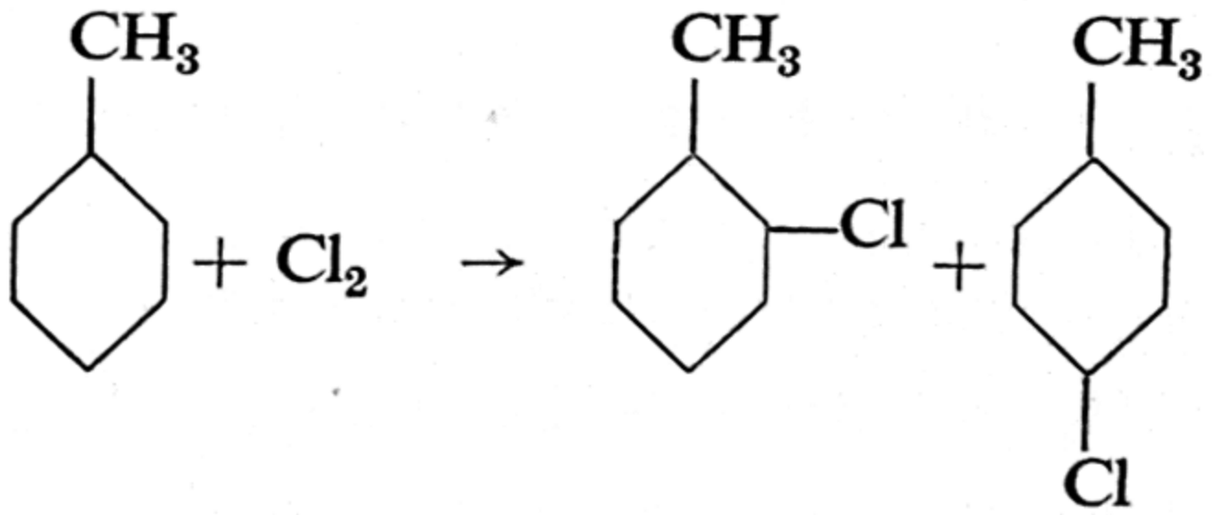
2. 4 dinitro-toluene

2. 4. 6 trinitro-toluene

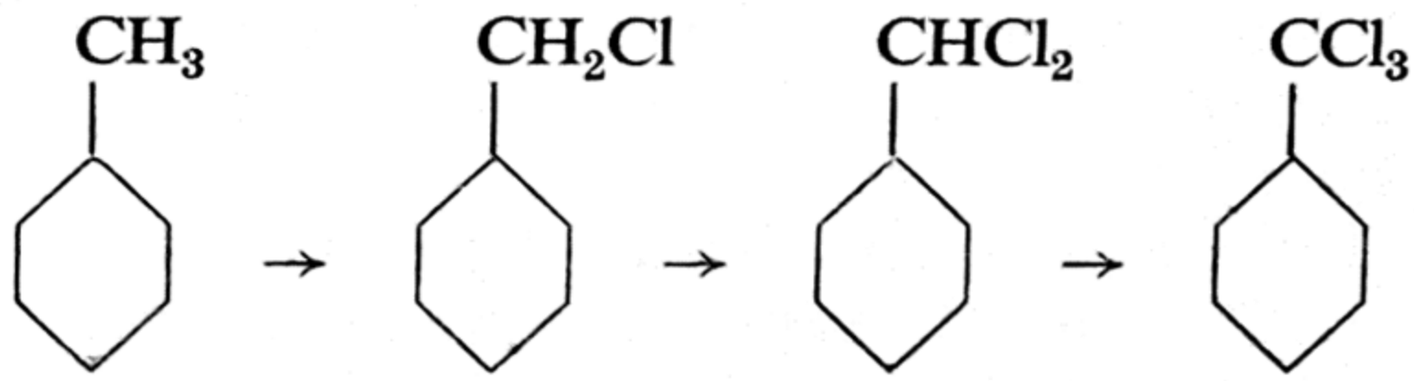
Note. In the further nitration of the mono-nitro to the di- and tri-nitro toluene, the ortho-para directing methyl group takes precedence over the meta directing nitro-group. This may be stated in general terms: if the benzene compound contains both an ortho-para directing substituent and also a meta directing substituent, then the former controls the course of any further substitution reaction.

Chlorination. The methyl group is not attacked by nitric acid, so that no complications due to this group results in the above nitration. Both the methyl group and the phenyl group (C_6H_5—) are, however, attacked by chlorine, and substitution may occur in either of these portions of the molecule depending on the conditions.

(*a*) When chlorine is passed into toluene in the cold in the presence of a halogen carrier, such as iodine or iron filings, substitution occurs in the nucleus to give a mixture of ortho- and para-chlorotoluene

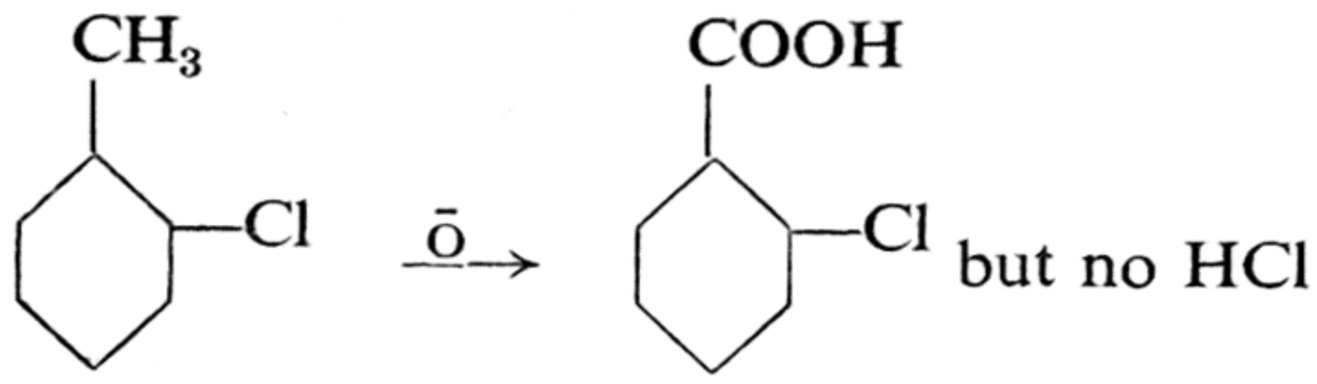


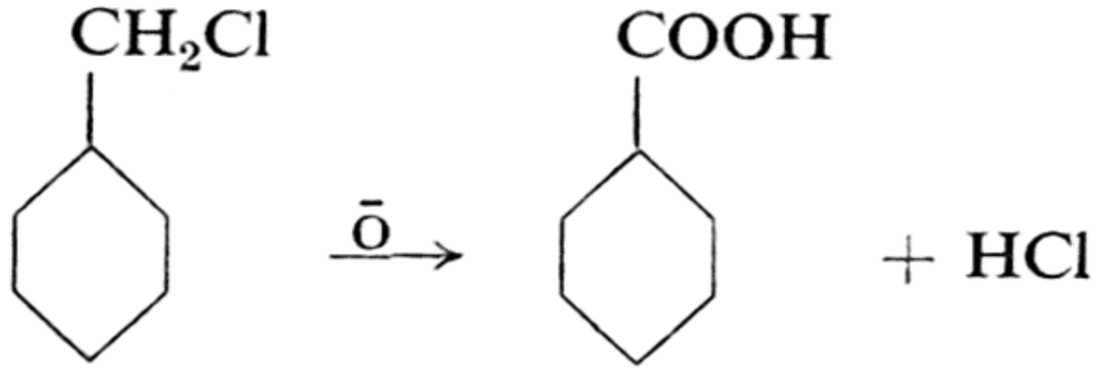
(*b*) When chlorine is passed into boiling toluene (in the absence of a halogen carrier, and preferably in direct sunlight), substitution occurs in the methyl group—



benzyl chloride benzal chloride benzo-trichloride

To determine whether the chlorine has entered the benzene ring or the side chain, all that is necessary is to oxidize a portion of the product, for example with acidified permanganate—





Thus, if hydrochloric acid is formed, the halogen must have been present in the side-chain and not in the benzene ring.

Oxidation. Toluene and other homologues of benzene are easily oxidized, the side-chain being ultimately replaced by the carboxyl (—COOH) group—

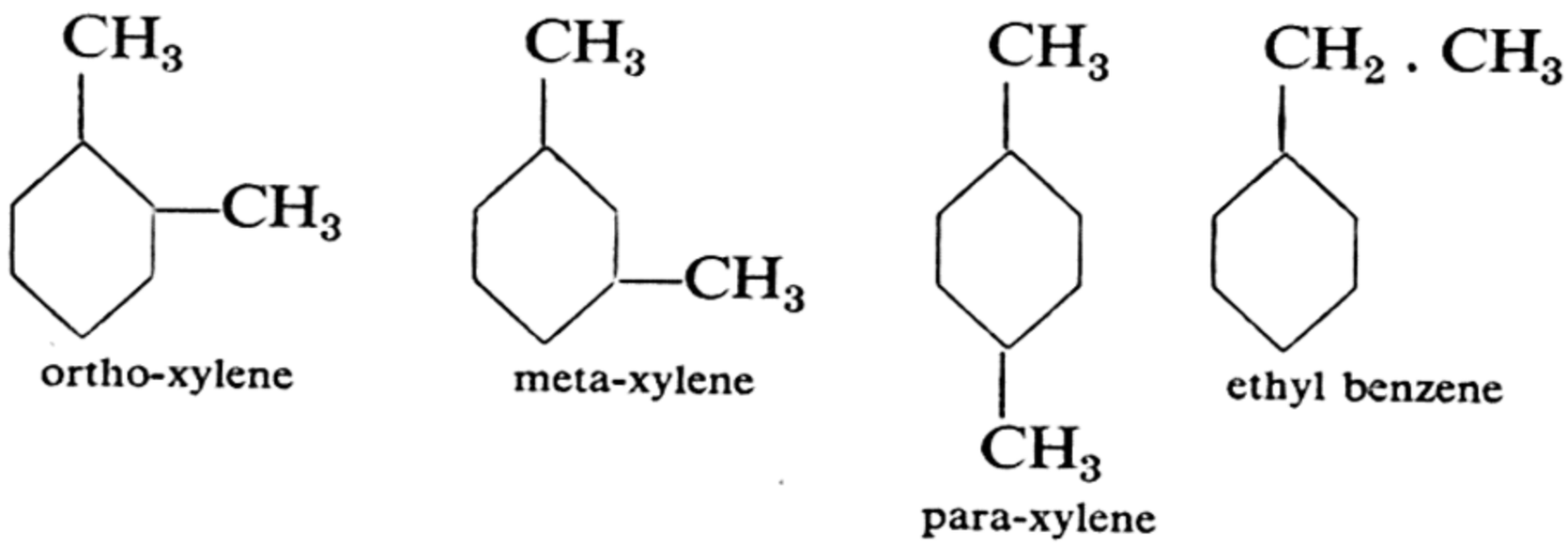
$$C_6H_5 . CH_3 \xrightarrow{O} C_6H_5 . CHOH \xrightarrow{O} C_6H_5 . CHO \xrightarrow{O} C_6H_5 . COOH$$

Suitable oxidizing agents include potassium permanganate and concentrated nitric acid, but occasionally potassium dichromate may be used. Sometimes the oxidation may be stopped at an intermediate stage, as in Etard's reaction in which the oxidizing agent is chromyl chloride.

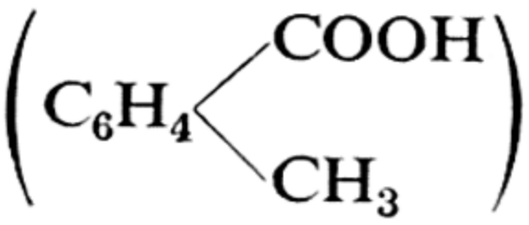
$$C_6H_5 . CH_3 + CrO_2Cl_2 \rightarrow C_6H_5 . CHO$$

benzaldehyde

Higher Homologues of Benzene

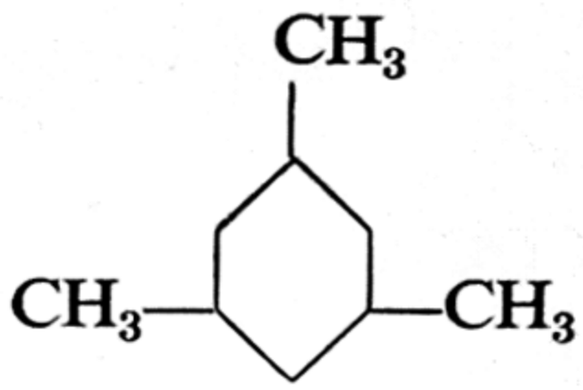


These xylenes on oxidation give o-, m- and p-toluic acids

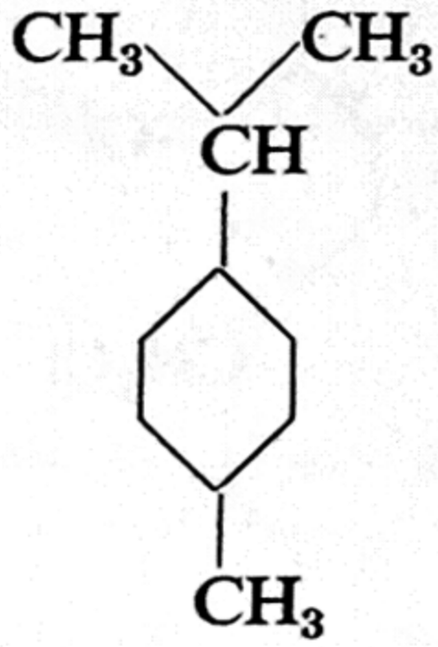


and on further oxidation the phthalic acids, $C_6H_4(COOH)_2$.

It is interesting to note that mesitylene (or, 1. 3. 5 trimethyl benzene) may be obtained from acetone by a condensation reaction when treated with sulphuric acid (*see* p. 921). Mesitylene and other homologues of benzene are usually obtained, however, from coal tar.



mesitylene



cymene

TABLE 121

Simpler Aromatic Hydrocarbons

Name	Formula	M.P. (°C)	B.P. (°C)
Benzene . . .	C_6H_6	+ 5·4	+ 80·5
Toluene . . .	$C_6H_5 . CH_3$	− 94	+ 110·0
o-Xylene . . .	$C_6H_4(CH_3)_2$	− 28	+ 142·0
p-Xylene . . .	$C_6H_4(CH_3)_2$	− 52	+ 139·0
m-Xylene . . .	$C_6H_4(CH_3)_2$	+ 15	+ 138·0
Mesitylene . . .	$C_6H_3(CH_3)_3$		+ 164·0
Cymene . . .	$CH_3 . C_6H_4CH(CH_3)_2$		+ 175·0

CHAPTER 36

AROMATIC HYDROCARBON DERIVATIVES

In the present chapter the more important derivatives of aromatic hydrocarbons are briefly reviewed. These include such classes of compounds as the nitro-compounds, amino-compounds, diazo-compounds, sulphonic acids, phenols, carboxylic acids, aromatic aldehydes and ketones. It should be noted that the homologues of benzene which have an aliphatic side-chain will show properties characteristic both of the aliphatic and aromatic portions of the molecule. In general, if the substituent is attached directly to the aliphatic side-chain its properties will resemble those of similar purely aliphatic compounds, but if the substituent is linked directly to the benzene portion of the molecule then somewhat different properties should be expected. Considering, for example, the halogen compounds, those which have the halogen substituted in the side-chain show the normal reactions of the alkyl halides, but those in which the halogen is substituted in the benzene ring are considerably less reactive. Thus, chlorobenzene is unaffected by water, dilute acids or alkalis, alcoholic potash, alcoholic ammonia, potassium cyanide, etc., whereas benzyl chloride, $C_6H_5CH_2Cl$, reacts in the same way as an alkyl chloride with these reagents.

SULPHONIC ACIDS

When aromatic hydrocarbons, or their derivatives, are treated with hot concentrated sulphuric acid, one of the hydrogen atoms of the benzene ring is replaced by the sulphonic acid group, $—SO_2OH$. Further substitution requires more vigorous conditions, for example, by means of fuming sulphuric acid.

$$C_6H_5 . \boxed{H + HO} . SO_2 . OH \rightarrow H_2O + C_6H_5 . SO_2OH$$

benzene sulphonic acid

Since the sulphonic acid group is meta-directing, further substitution will occur only slowly to give benzene-m-disulphonic acid.

Properties. The sulphonic acids are often hygroscopic and are all freely soluble in water. This solubility in water is in fact one of the most important properties of the sulphonic acids, since it provides a convenient means of converting an insoluble aromatic compound into one which is water soluble. Benzene-sulphonic acid forms colourless crystals, very readily soluble in water and in alcohol, and may be prepared by heating

a mixture of equal volumes of benzene and concentrated sulphuric acid on a water-bath until all the benzene has disappeared.

The chemical properties of the sulphonic acids are illustrated by the following reactions.

1. When heated with concentrated hydrochloric acid (under pressure) at about 150°C, or by the action of superheated steam, the sulphonic acid group is replaced by hydrogen to form the hydrocarbon—

$$C_6H_5 . SO_2OH + HO{-}H \rightarrow C_6H_6 + H_2SO_4$$

2. Fusion with alkalis converts the sulphonic acid (or their salts) into the corresponding hydroxy-compound—

$$C_6H_5 . SO_2OK + KOH \rightarrow K_2SO_3 + \underset{\text{phenol}}{C_6H_5OH}$$

3. When heated with potassium cyanide sulphonic acid salts are converted into the corresponding nitrile, and the latter may be converted into the corresponding carboxylic acid by hydrolysis or into the amino-compound by reduction—

$$C_6H_5 . SO_2OK \xrightarrow{KCN} C_6H_5 . CN \begin{cases} \xrightarrow{H_2O} \underset{\text{benzoic acid}}{C_6H_5COOH} \\ \xrightarrow{H} \underset{\text{benzylamine}}{C_6H_5 . CH_2NH_2} \end{cases}$$

4. With phosphorus pentachloride, sulphonic acids are converted into the important sulphonyl chlorides—

$$C_6H_5 . SO_2OH + PCl_5 \rightarrow HCl + POCl_3 + \underset{\substack{\text{benzene sulphonyl} \\ \text{chloride}}}{C_6H_5 . SO_2Cl}$$

These react with ammonia or ammonium carbonate to form sulphonamides, which usually crystallize easily and hence are useful in the identification of an unknown sulphonic acid.

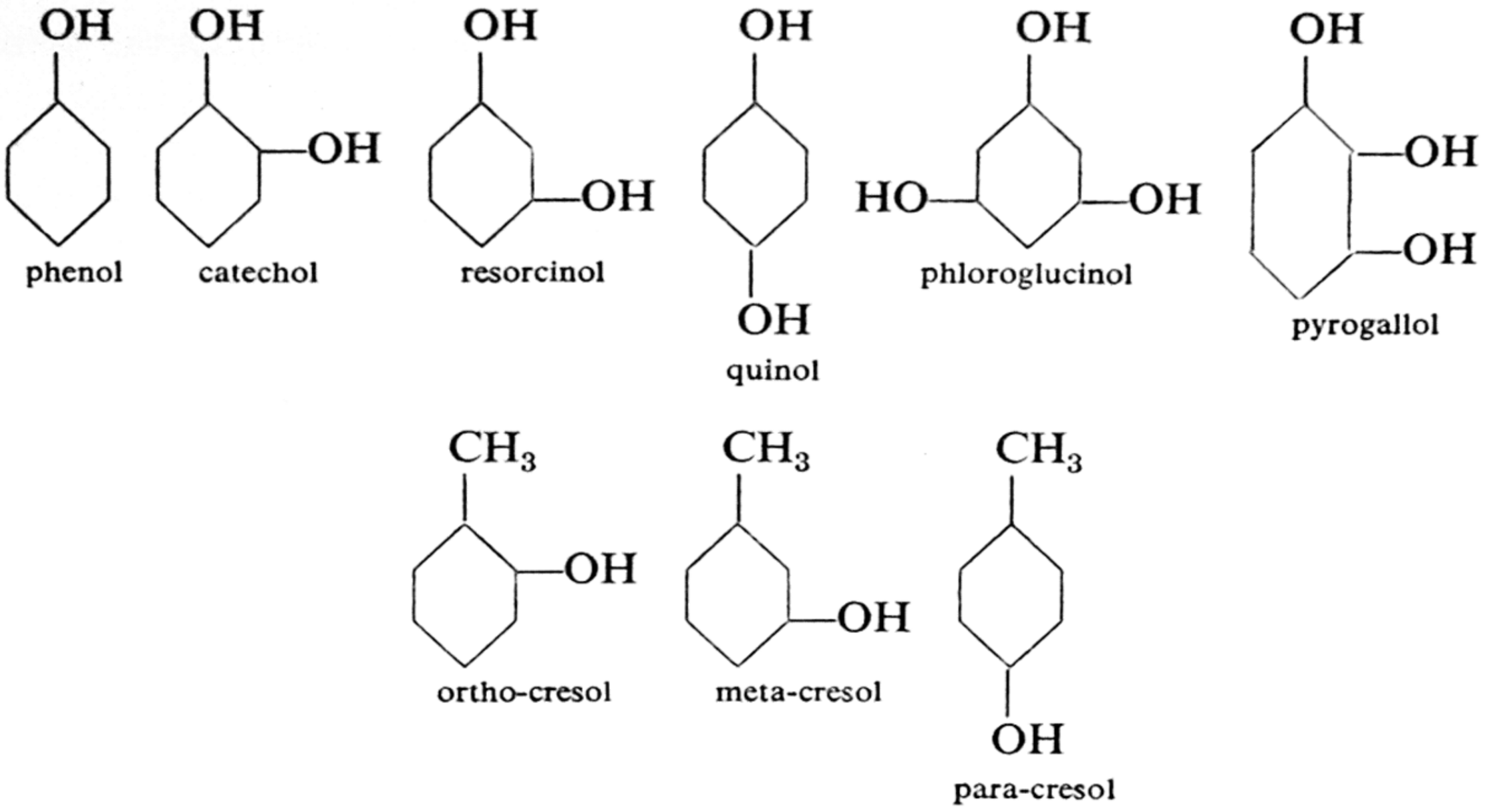
$$C_6H_5 . SO_2Cl \ (+ NH_3) \rightarrow \underset{\text{benzene sulphonamide}}{C_6H_5 . SO_2NH_2}$$

Sulphonyl chlorides are reduced to sulphinic acids and mercaptans—

$$C_6H_5 . SO_2Cl \xrightarrow{H} \underset{\text{benzene sulphinic acid}}{C_6H_5 . SO . OH} \xrightarrow{H} \underset{\text{phenyl mercaptan}}{C_6H_5 . SH}$$

PHENOLS

The phenols are the aromatic counterpart of the aliphatic alcohols, and contain one or more hydroxyl groups directly attached to a benzene ring.



Phenol is obtained commercially from the middle-oil distillation fraction of coal-tar. It may also be obtained chemically by fusing sodium benzene sulphonate with sodium hydroxide, or from aniline via the diazo-reaction (*see* p. 1014)—

$$C_6H_5 . SO_2ONa + NaOH \rightarrow C_6H_5OH + Na_2SO_3$$

$$C_6H_5 . NH_2 \text{ (via diazo-reaction)} \rightarrow C_6H_5 . N_2Cl \xrightarrow[\text{boil}]{} C_6H_5OH$$

Properties. Phenol is a colourless crystalline solid (m.p. 43°C, b.p. 182°C), and has a characteristic disinfectant-like smell. It is only moderately soluble in water at ordinary temperatures, but is completely miscible with water above 68°C, the critical solution temperature. On exposure to air it slowly evaporates, and on exposure to light develops a slight pink colour due to impurities. A solution of phenol in water has antiseptic properties, but it is not advisable to handle the solid since it may cause blistering.

Chemical Reactions

1. Phenol dissolves easily in aqueous sodium hydroxide to form sodium phenate, C_6H_5ONa. Phenol is in fact an acid, but only a very weak one. Thus sodium phenate is hydrolyzed by water and is completely decomposed by carbon dioxide to reform phenol. This latter reaction, which indicates that phenol is more weakly acidic than carbonic acid, is often used to separate phenol from a more strongly acidic compound such as benzoic acid.

Treatment of the mixture of acids with sodium hydroxide gives sodium

phenate and sodium benzoate. The aqueous solution is then treated with carbon dioxide—

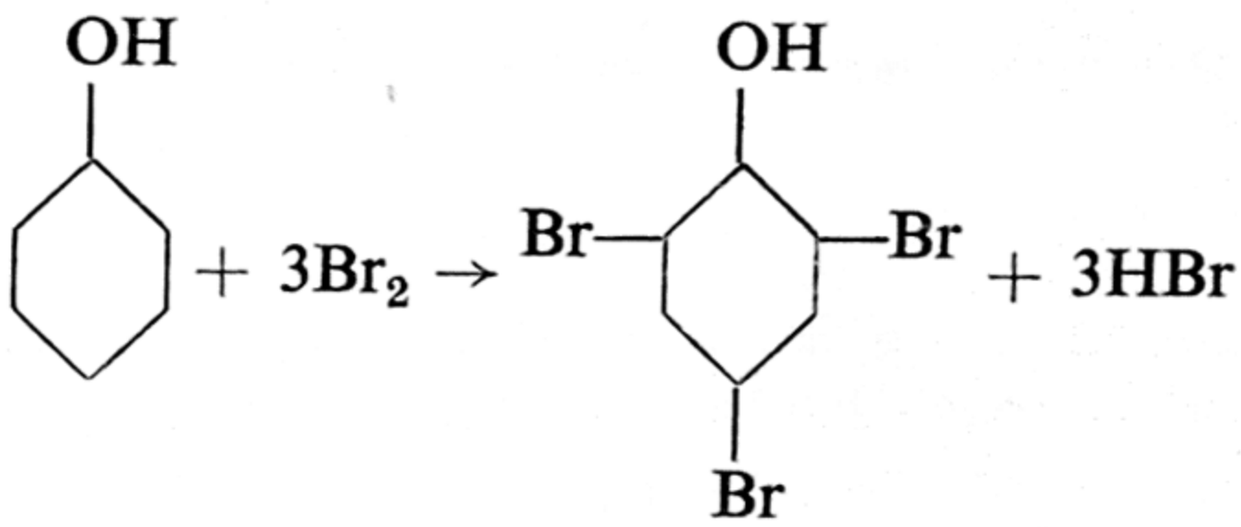
$$C_6H_5COONa + CO_2 \text{ (no reaction)}$$

$$2C_6H_5ONa + CO_2 + H_2O \rightarrow Na_2CO_3 + 2C_6H_5OH$$

2. When phenol is heated in a closed tube with zinc dust, it is reduced to benzene—

$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$$

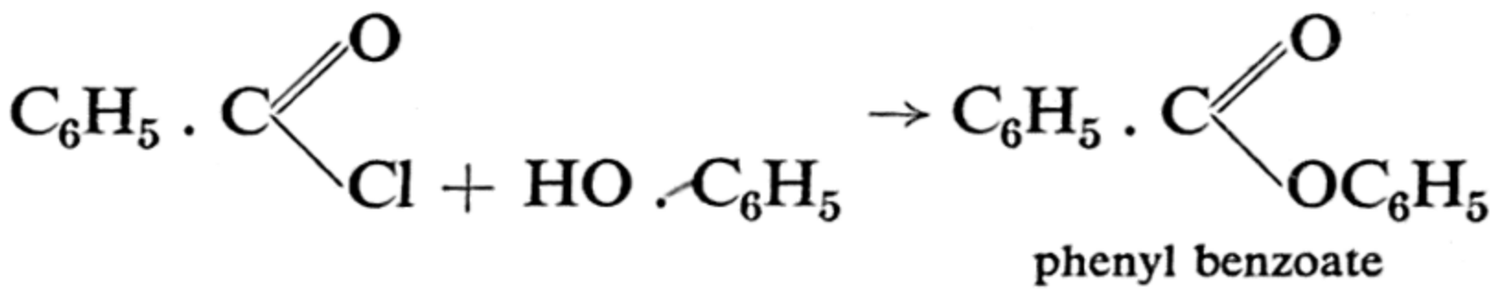
3. When an aqueous solution of phenol is shaken with bromine-water, even at ordinary temperatures, reaction occurs to form a white precipitate of 2.4.6. tribromo-phenol—



This latter reaction indicates both the ortho-para directing properties of the OH group, and also that ortho-para substitution reactions occur in general quite easily. This bromination reaction is sometimes used commercially in extracting bromine from its aqueous solutions.

4. Ortho- and para-nitrophenol may be prepared by the action of dilute nitric acid on phenol at moderate temperatures. Steam-distillation serves to remove the ortho-nitrophenol.

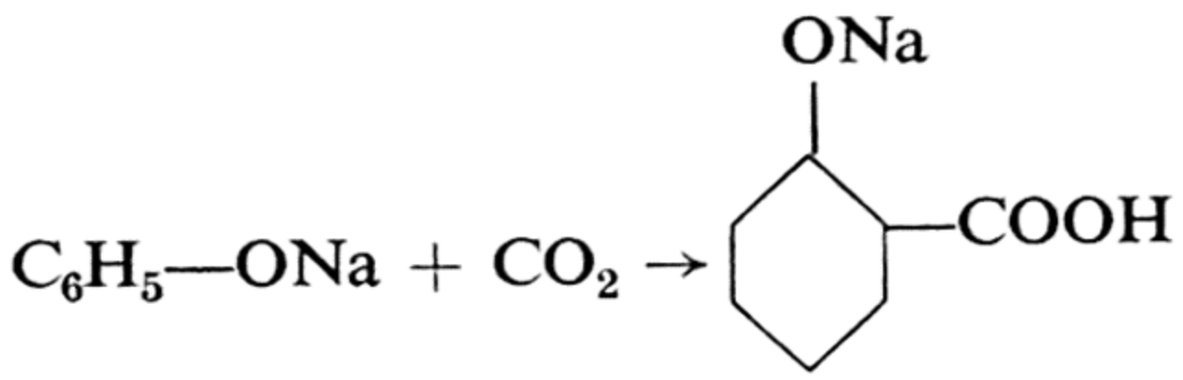
5. *Schotten-Baumann Reaction.* The benzoyl ester of phenol may be prepared by dissolving phenol in aqueous sodium hydroxide, adding a small excess of benzoyl chloride and shaking the mixture—



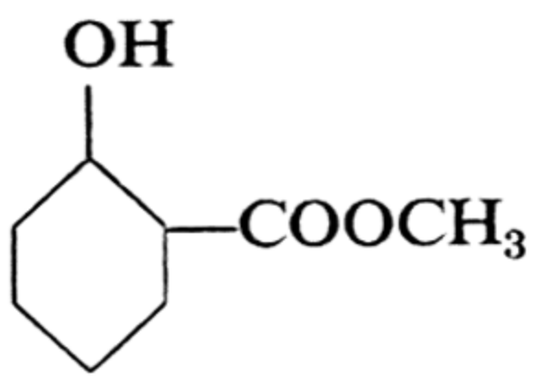
phenyl benzoate

A similar reaction occurs with aniline in the place of phenol to form benzoyl-aniline (or benz-anilide)—$C_6H_5CONHC_6H_5$. The reaction is based on the fact that benzoyl chloride is only very slowly hydrolyzed by water, so that the reaction can be carried out easily in aqueous solution. Acetyl chloride and acetic anhydride on the other hand are so readily hydrolyzed by water that acetylation (that is, the introduction of the CH . CO— group) by these reagents must necessarily be carried out in the absence of water.

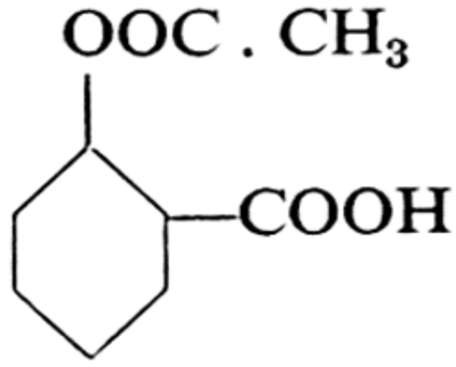
6. *Kolbe's Reaction.* When phenol is converted by treatment with sodium hydroxide into sodium phenate, and the latter, after drying, is heated to about 200°C in a stream of carbon dioxide, the sodium salt of salicylic acid is formed—



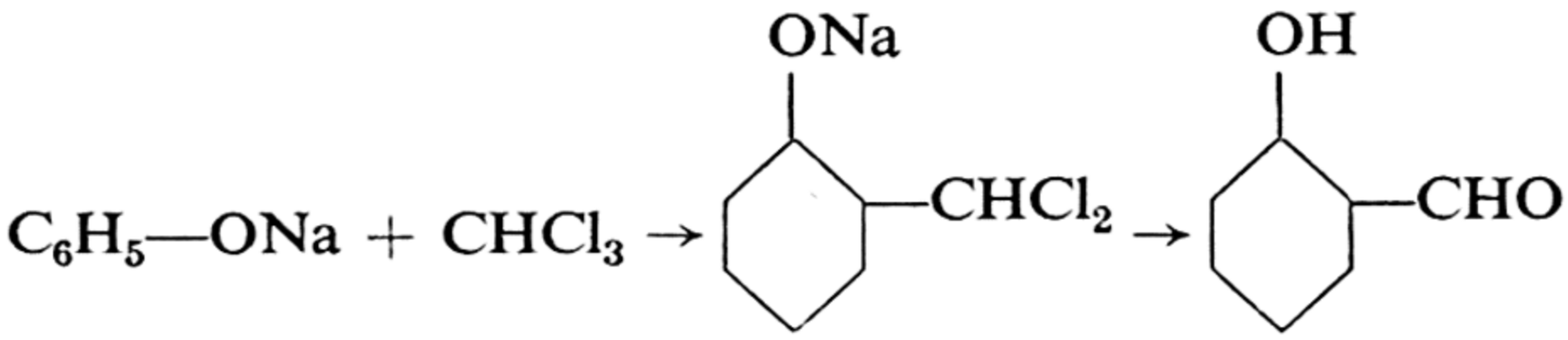
Methyl salicylate, present in Oil of Wintergreen, is



that is, the methyl ester of salicylic acid. Aspirin is acetyl-salicylic acid

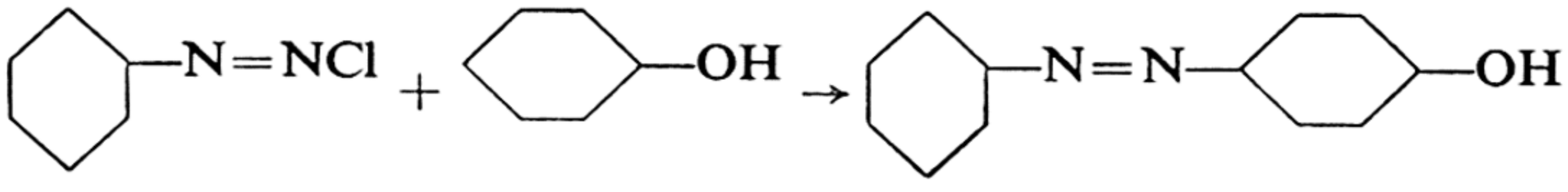


7. *Reimer-Tiemann Reaction.* Phenolic aldehydes may be prepared by heating phenols with chloroform in alkaline solution. The main product is the ortho-compound, but small quantities of the para-compound are formed at the same time—

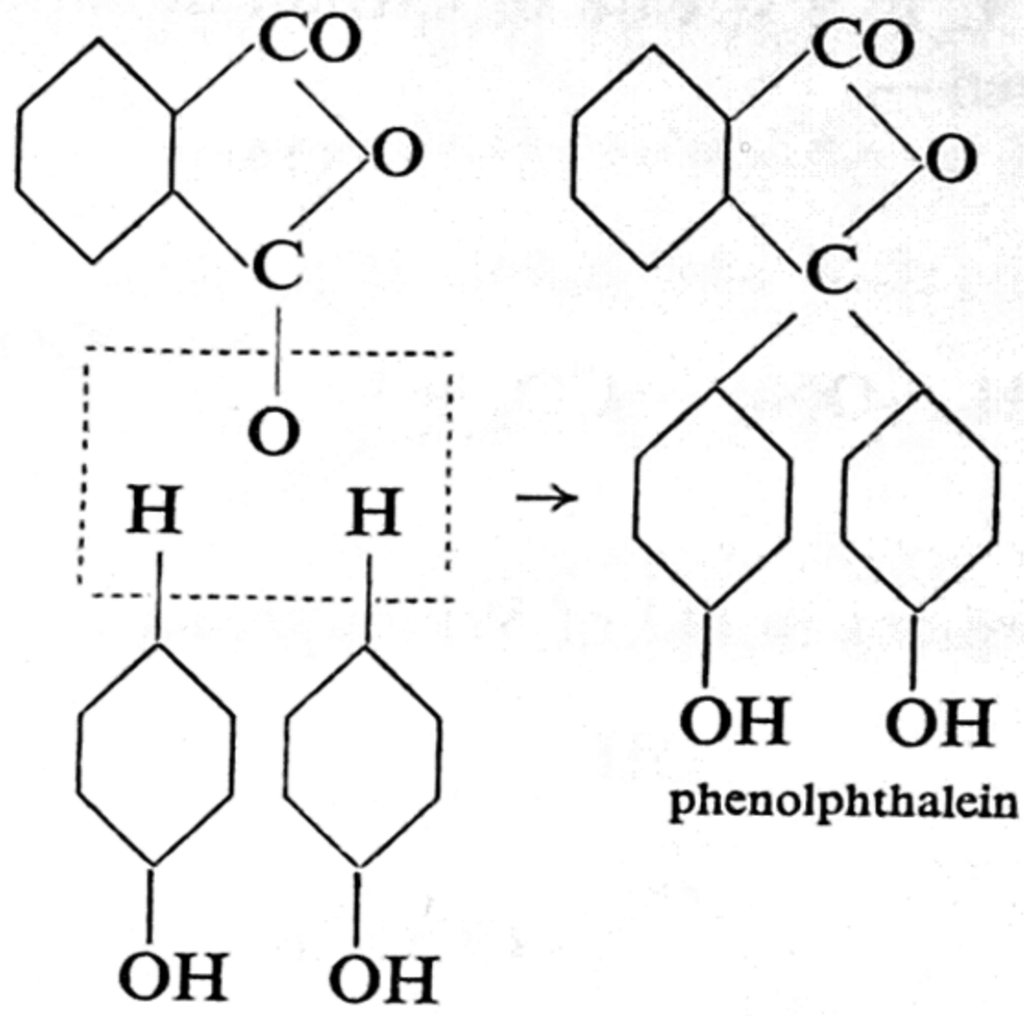


If carbon tetrachloride is used instead of chloroform, the product is mainly salicylic acid.

8. *Coupling Reactions* (*see* p. 1017). The following coupling reaction occurs on adding phenol to a diazonium salt—



9. Phenol will also undergo a condensation reaction with phthalic anhydride in the presence of a suitable dehydrating agent—



phenolphthalein

Tests for Phenol. In addition to the above reactions, phenol may be detected by such reactions as—

Liebermann's "nitroso" reaction. This test is based on the colour changes which occur in the formation of p-nitroso phenol. A few small crystals of phenol are treated in a test-tube with a little sodium nitrate and 2–3 ml concentrated sulphuric acid. The brown coloured mixture changes to a bluish-green or intense blue colour on warming. When the product is poured into water the colour changes to red, but on adding alkali a further colour change to blue occurs. This reaction is often used in the reverse sense of using a phenol to detect the presence of a nitroso-compound.

Most phenols give a characteristic colour with aqueous ferric chloride. Phenol, resorcinol, o-, m- and p-cresols, for example, give violet or blue colorations.

The Phenolic OH. In concluding this section, it is well to remember that the OH group in phenol does not resemble the alcoholic hydroxyl group. Thus phenol, in addition to being an acid, does not react with hydriodic acid, shows only slight reaction with phosphorus pentachloride, does not dehydrate with concentrated sulphuric acid and does not undergo the usual esterification reactions.

Uses of Phenol. Considerable quantities of phenol are nowadays required for the manufacture of phenolic resins and plastics, among which may be mentioned the Bakelite resins and plastics. These are prepared by a condensation reaction between phenol and formaldehyde in the presence of a suitable catalyst (ammonia, acid, or alkali) under carefully controlled conditions.

Smaller quantities of phenol are used in the manufacture of aspirin,

phenacetin and similar drugs, and in weak aqueous solution as a disinfectant.

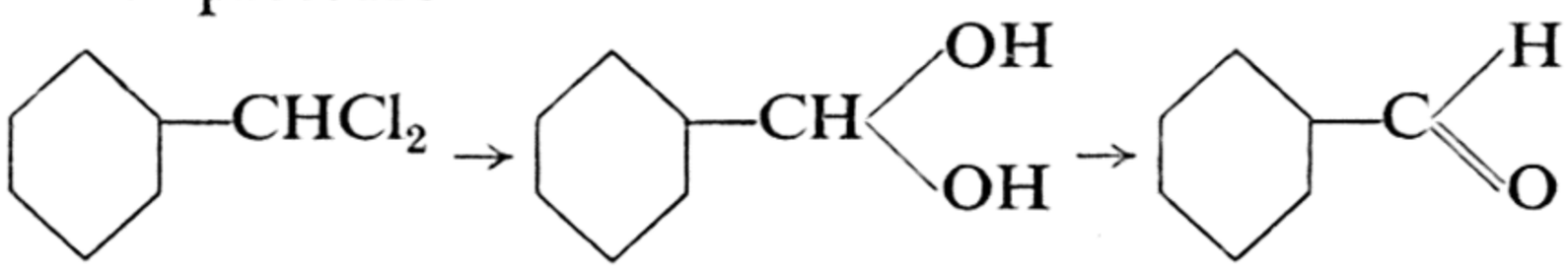
AROMATIC ALDEHYDES

The purely aromatic aldehydes resemble aliphatic aldehydes very closely both in their methods of preparation and in their properties. Certain of the latter are however different, but these will be discussed in some detail later in this section.

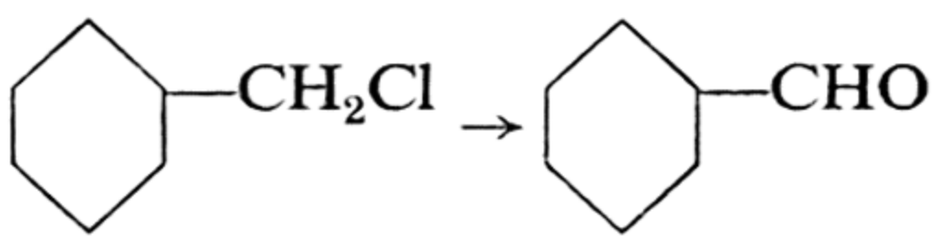
Benzaldehyde, C_6H_5 . CHO. Benzaldehyde occurs naturally in amygdalin, a glucoside present in bitter almonds. Hydrolysis of the amygdalin, either via the enzyme emulsin present in bitter almonds or via dilute acid, liberates the benzaldehyde—

$$C_{20}H_{27}O_{11}N + 2H_2O \rightarrow 2C_6H_{12}O_6 + HCN + C_6H_5 . CHO$$

Preparation. Commercially, benzaldehyde is prepared either by oxidation of toluene or by the hydrolysis of benzal chloride, $C_6H_5CHCl_2$. The latter, prepared by chlorinating toluene, is heated with milk-of-lime in an autoclave under pressure—



Benzaldehyde is also obtained commercially by heating benzyl chloride with aqueous copper nitrate or lead nitrate



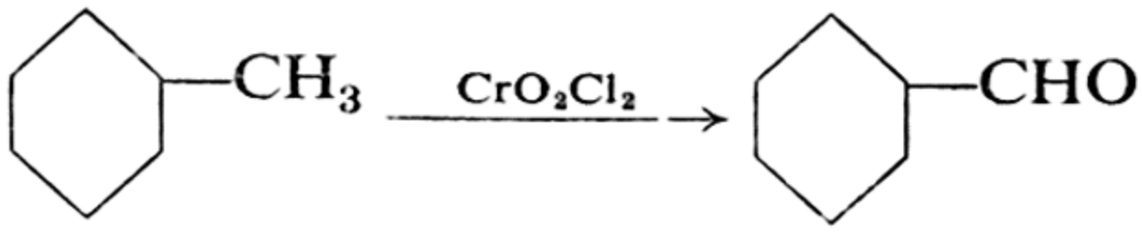
Other methods of general interest include—

(*a*) The oxidation of benzyl alcohol, $C_6H_5 . CH_2OH$.

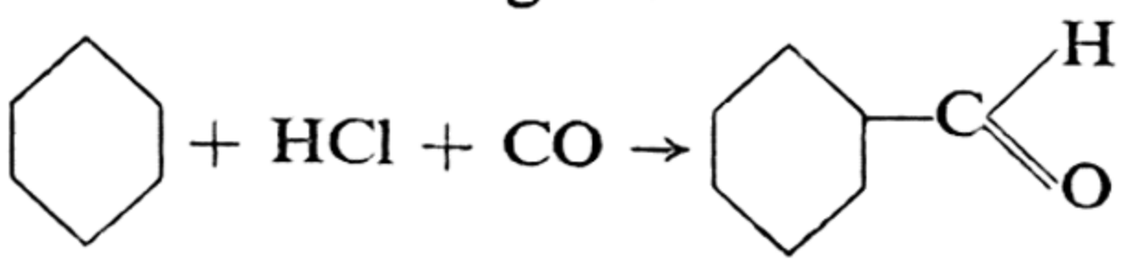
(*b*) Distilling a mixture of the calcium salts of benzoic and formic acids—

$$(C_6H_5 . COO)_2Ca + (H . COO)_2Ca \rightarrow 2C_6H_5 . CHO + 2CaCO_3$$

(*c*) *Etard's reaction*, which involves oxidizing toluene with chromyl chloride in carbon disulphide solution.



(*d*) *Gattermann's Reaction.* Dry benzene is treated with anhydrous aluminium chloride and, after passing in a little dry HCl, a steady stream of carbon monoxide is bubbled through the solution.



(*e*) The treatment of benzonitrile, $C_6H_5 . CN$, with dry stannous chloride and dry hydrogen chloride in ethereal solution—

$$C_6H_5 . C{\equiv}N \xrightarrow{H} C_6H_5 . CH{=}NH \xrightarrow{H_2O} C_6H_5 . CHO + NH_3$$

(*f*) The reduction of benzoyl chloride with hydrogen in the presence of palladized barium sulphate as catalyst—

$$C_6H_5 . C(=O)Cl \xrightarrow{H_2} C_6H_5 . C(=O)H + HCl$$

Properties. Benzaldehyde is a colourless liquid, b.p. 179°C, with a characteristic odour of almonds. It is readily soluble in alcohol and ether but is only sparingly soluble in water.

Chemically, benzaldehyde shows most of the usual reactions of aliphatic aldehydes. These include ease of oxidation to benzoic acid, reduction with sodium amalgam to benzyl alcohol, addition reactions with sodium bisulphite and hydrogen cyanide, and condensation reactions with hydroxylamine and hydrazines (*see* p. 910). Benzaldehyde is very easily oxidized to benzoic acid and bottles of benzaldehyde on exposure to air and sunlight often contain crystals of this acid. This ease of oxidation is also revealed by the reducing action of benzaldehyde on ammoniacal silver nitrate (silver mirror test). It only slowly, however, restores the colour to Schiff's reagent and does not reduce Fehling's solution.

The principal differences between aliphatic and aromatic aldehydes are shown in the following reactions of benzaldehyde—

(i) *With ammonia*, instead of forming the expected aldehyde-ammonia, benzaldehyde undergoes a condensation reaction to form hydrobenzamide

$$3C_6H_5 . CHO + 2NH_3 \rightarrow \begin{matrix} C_6H_5 . CH \\ \\ C_6H_5 . CH \\ \\ C_6H_5 . CH \end{matrix} \begin{matrix} \\ \diagup\!\!=\!\!\diagdown N \\ \\ \diagdown\!\!=\!\!\diagup N \\ \\ \end{matrix} + 3H_2O$$

The latter may be converted back to benzaldehyde by the action of mineral acids, or may be reduced to give a mixture of dibenzylamine, $(C_6H_5 . CH_2)_2NH$, and benzylamine, $C_6H_5 . CH_2 . NH_2$.

(ii) *With an alcoholic solution of potassium cyanide*, on heating, the *Benzoin Condensation* reaction occurs—

$$\begin{matrix} C_6H_5 . CHO \\ \\ C_6H_5 . CHO \end{matrix} \rightarrow \begin{matrix} C_6H_5 . C(H)(OH) \\ | \\ C_6H_5 . C{=}O \end{matrix}$$

benzoin

With oxidizing agents, the latter may be converted into the di-ketone benzil, $C_6H_5 . CO . CO . C_6H_5$.

(iii) *Cannizzaro's Reaction.* When benzaldehyde is treated with aqueous alkali the following reaction occurs slowly on standing or more rapidly on warming—

$$2C_6H_5 . CHO + NaOH \rightarrow C_6H_5 . COONa + C_6H_5 . CH_2OH$$

This reaction is not however peculiar to aromatic aldehydes. Formaldehyde and many other aliphatic aldehydes which do not resinify with sodium hydroxide show a similar reaction.

$$2H . CHO + NaOH \rightarrow H . COONa + CH_3OH$$

(iv) *Claisen Reaction.* In the presence of a little sodium hydroxide, benzaldehyde undergoes a condensation reaction with other aldehydes and ketones which contain the group $—CH_2—CO—$

$$C_6H_5 . CHO + CH_3 . CHO \rightarrow C_6H_5—CH=CH—CHO$$

cinnamic aldehyde

(v) *Perkin's Reaction*, for preparing aromatic acids containing an unsaturated side-chain, is a modification of this reaction. Thus in the Perkin synthesis of cinnamic acid, benzaldehyde is heated to about 180°C with a mixture of sodium acetate and acetic anhydride—

$$C_6H_5 . CHO + CH_3 . COOH \rightarrow C_6H_5—CH=CH—COOH$$

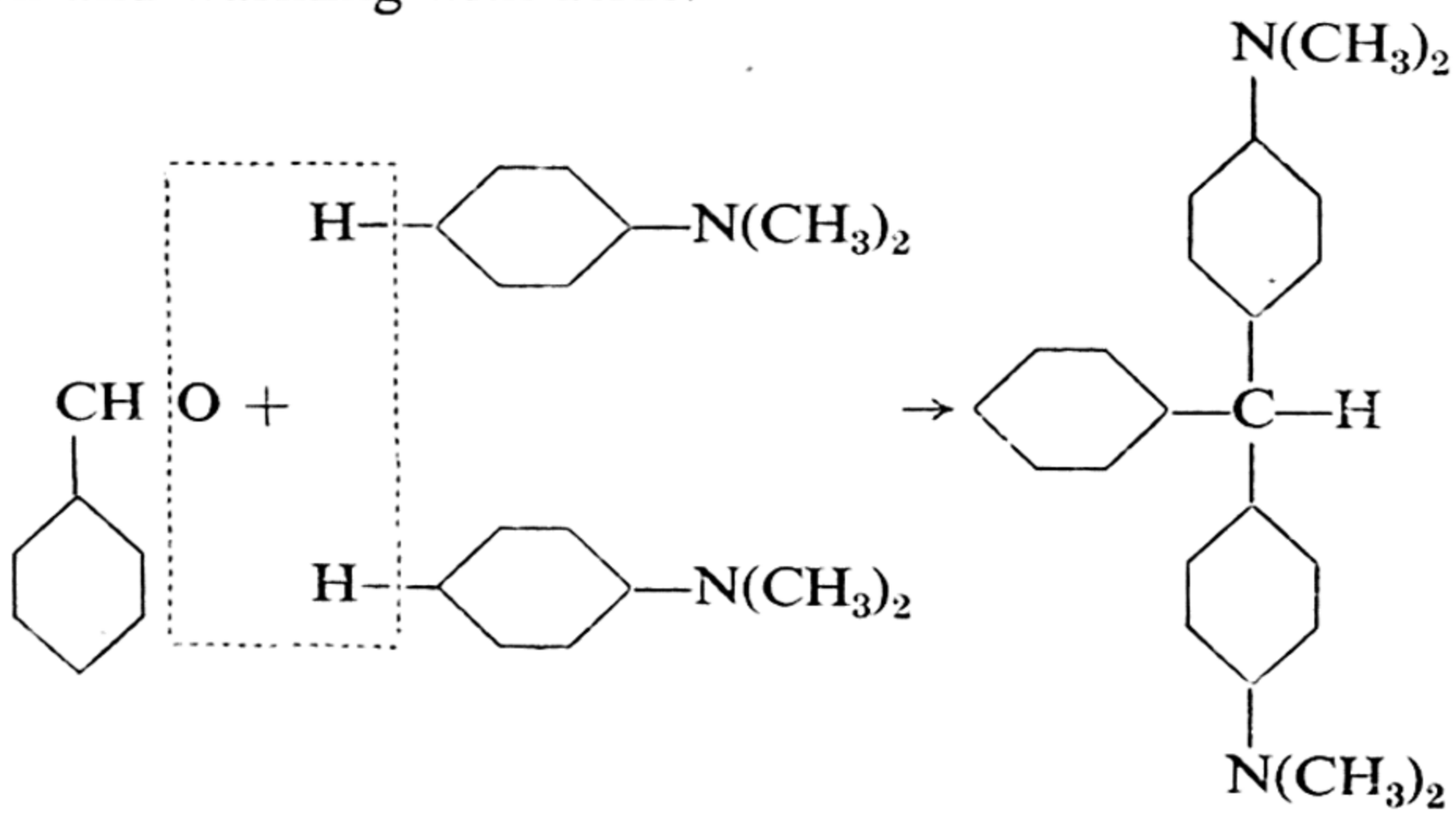
cinnamic acid

(vi) When *heated with aniline* (and other primary amines), benzaldehyde reacts to form benzylidene-aniline or Schiff's base—

$$C_6H_5 . CHO + H_2N . C_6H_5 \rightarrow C_6H_5—CH=N—C_6H_5$$

Schiff's base

(vii) When *heated with dimethyl-aniline* in the presence of zinc chloride, a triphenyl methane derivative is formed which is known as *Malachite Green* base. Malachite Green is a particular member of the triphenyl methane dyestuffs, and may be prepared from the above compound by oxidation and warming with acids.



Other reactions. The —CHO group is meta-directing, and direct nitration of benzaldehyde produces mainly meta-nitrobenzaldehyde. Para-nitrobenzaldehyde may be prepared from para-nitrotoluene by Etard's reaction, and the ortho-nitrobenzaldehyde by nitrating cinnamic acid and subsequently oxidizing the —CH=CH—COOH group to —CHO.

AROMATIC KETONES

$C_6H_5 . CO . CH_3$ acetophenone

$C_6H_5 . CO . C_6H_5$ benzophenone

Preparation of Aromatic Ketones. These compounds may be obtained by distilling the calcium salt of the corresponding acid, or the mixed calcium salts.

$$(C_6H_5 . COO)_2Ca \rightarrow C_6H_5 . CO . C_6H_5 + CaCO_3$$

$$(C_6H_5 . COO)_2Ca + (CH_3 . COO)_2Ca \rightarrow 2C_6H_5 . CO . CH_3 + 2CaCO_3$$

Friedel and Craft's reaction—the action of acetyl chloride on dry benzene containing an excess of freshly prepared anhydrous aluminium chloride—also gives rise to the formation of acetophenone.

$$C_6H_6 + AlCl_3 + CH_3 . COCl \rightarrow C_6H_5 . CO . CH_3$$

Properties. Acetophenone forms colourless crystals, m.p. about 20°C, which are moderately soluble in water (acetone is completely soluble). Under carefully controlled conditions, acetophenone may be oxidized with cold potassium permanganate to benzoyl formic acid, $C_6H_5 . CO . COOH$, which on further oxidation forms benzoic acid. Acetophenone forms oximes, phenylhydrazones and cyanhydrins, but under ordinary conditions, it does not form a bisulphite compound.

Benzophenone occurs in two crystalline forms, m.p. 49° and 26°C. It is less reactive than acetophenone, and on reduction gives the important compound diphenyl-methane—

$$C_6H_5 . CO . C_6H_5 \rightarrow C_6H_5 . CH_2 . C_6H_5$$

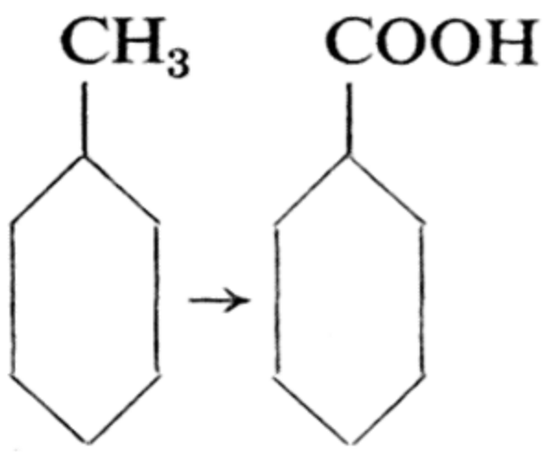
diphenylmethane

AROMATIC ACIDS

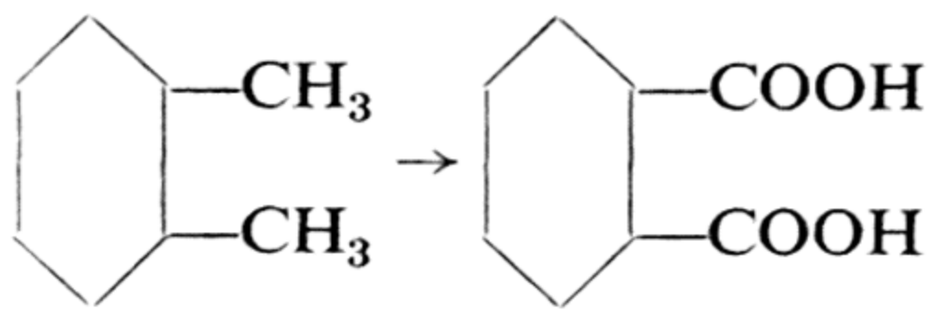
The aromatic carboxylic acids are those compounds in which the —COOH group is directly linked to the benzene nucleus. In their properties, they behave very much like aliphatic carboxylic acids, except in so far as these may be modified by the reactions of the benzene ring portion of the molecule.

Preparation. The following methods are available for obtaining the aromatic acids.

1. Oxidation of benzene derivatives which contain one or more carbon side-chains in the molecule—



toluene benzoic acid



o-xylene phthalic acid

2. Hydrolysis of benzo-nitrile, C_6H_5 . CN. The latter may be prepared—

(*a*) by distilling a salt such as C_6H_5 . SO_2OK with KCN;
(*b*) by the Sandmeyer reaction (*see* p. 1016);
(*c*) by dehydrating benzaldoxime, for example, with acetic anhydride

$$C_6H_5—CH=NOH—H_2O \rightarrow C_6H_5 . CN$$

3. From the Grignard reagent, C_6H_5MgI, by reaction with carbon dioxide—

$$C_6H_5MgI + CO_2 + H_2O \rightarrow C_6H_5 . COOH + Mg(OH)I$$

4. Via Kolbe's reaction (*see* p. 997).

5. Via the Reimer-Tiemann reaction using carbon tetrachloride in place of chloroform (*see* p. 997).

6. From sodium benzene sulphonate by heating with sodium formate—

$$C_6H_5 . SO_2ONa + H . COONa \rightarrow C_6H_5 . COONa + NaHSO_3$$

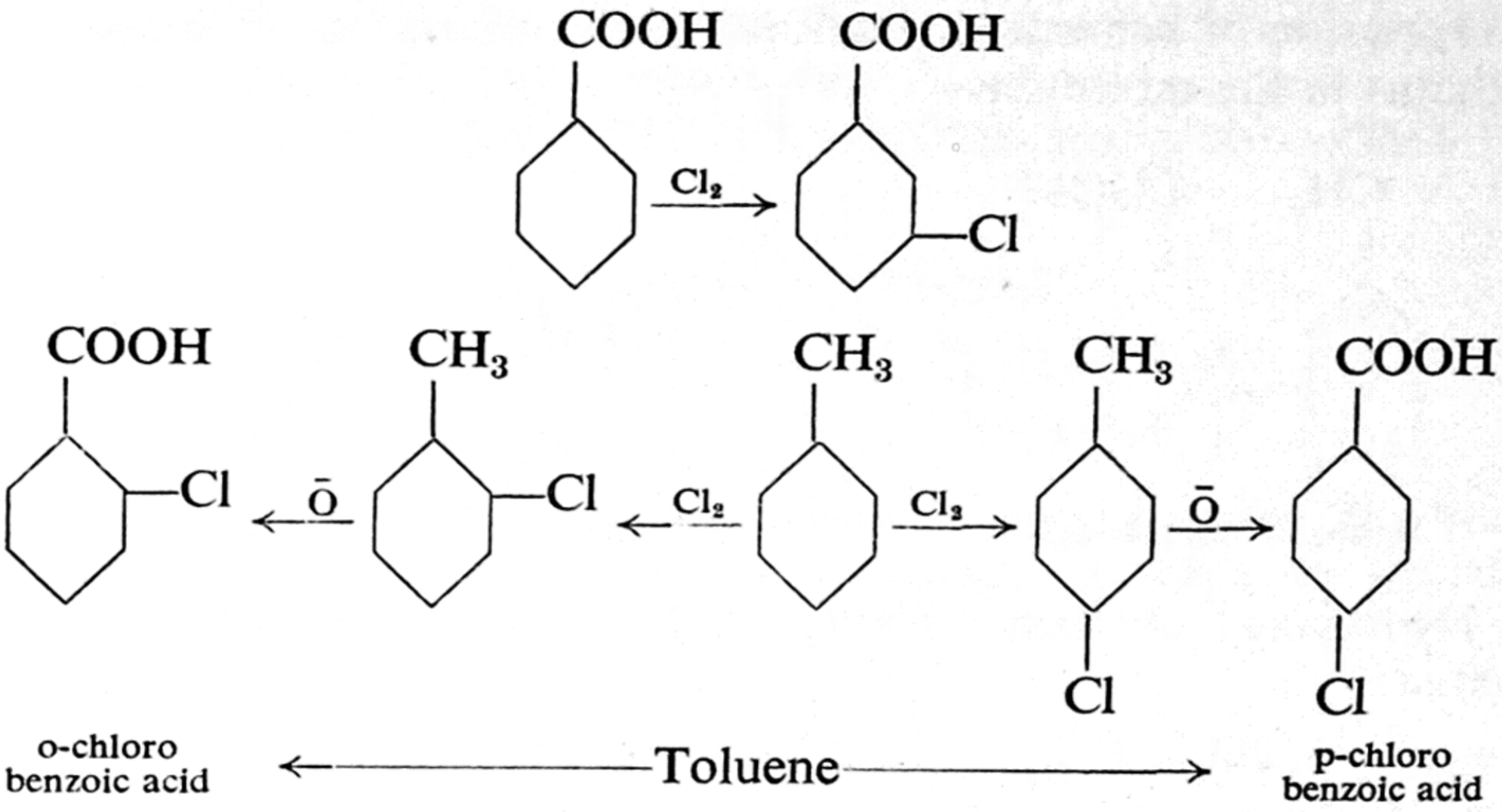
Properties. Benzoic acid occurs naturally in gum benzoin (a natural resin), and was originally obtained from this substance by heating, when the benzoic acid sublimed off. It is a white crystalline compound, m.p. 121°C, sublimes when heated rapidly and is volatile in steam. It is only sparingly soluble in cold water, but dissolves readily in hot water (from which it crystallizes on cooling) and also in dilute sodium hydroxide and sodium carbonate solutions.

When heated with lime, benzoic acid is converted to benzene—

$$C_6H_5 . COOH + CaO \rightarrow C_6H_6 + CaCO_3$$

Since the —COOH group is meta-directing, nitration, sulphonation or halogenation of benzoic acid gives mainly the meta-substituted compound.

The ortho- and para-derivatives may, however, be prepared indirectly from toluene—



Derivatives of Benzoic Acid

Benzoyl Chloride, $C_6H_5 . COCl$, is a colourless liquid with a pungent lachrymatory smell. It may be prepared from benzoic acid by the normal reaction with phosphorus pentachloride or phosphorus oxychloride—

$$C_6H_5 . COOH + PCl_5 \rightarrow C_6H_5 . COCl + POCl_3 + HCl$$

It does not react with water nor with aqueous sodium hydroxide at ordinary temperatures. This lack of reactivity towards water contrasts strongly with the vigorous reactivity of acetyl chloride, and explains the use of the former in the Schotten-Baumann reaction for preparing benzoyl esters.

Benzoyl Esters, e.g. ethyl benzoate, $C_6H_5 . COOC_2H_5$. These are best prepared by the *Schotten-Baumann reaction*, which uses benzoyl chloride in the presence of aqueous sodium hydroxide to introduce the benzoyl group into hydroxy and amino-compounds—

$$C_6H_5 . COCl + NaOH + C_2H_5OH \rightarrow C_6H_5 . COOC_2H_5 + NaCl + H_2O$$

Ethyl benzoate is a colourless liquid with a peppermint-like odour.

Benzoic Anhydride, $(C_6H_5 . CO)_2O$, may be prepared by the action of benzoyl chloride on sodium benzoate—

$$C_6H_5 . COCl + C_6H_5 . COONa \rightarrow (C_6H_5 . CO)_2O + NaCl$$

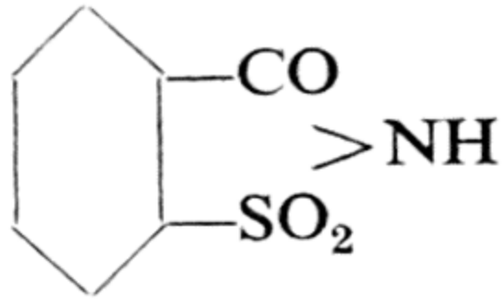
or, simply, by pouring benzoyl chloride into aqueous pyridine or sodium carbonate solution. It is a colourless crystalline solid, m.p. 40°C, b.p. about 350°C.

Benzamide, $C_6H_5 . CONH_2$, may be prepared by the action of dilute aqueous ammonia on benzoyl chloride—

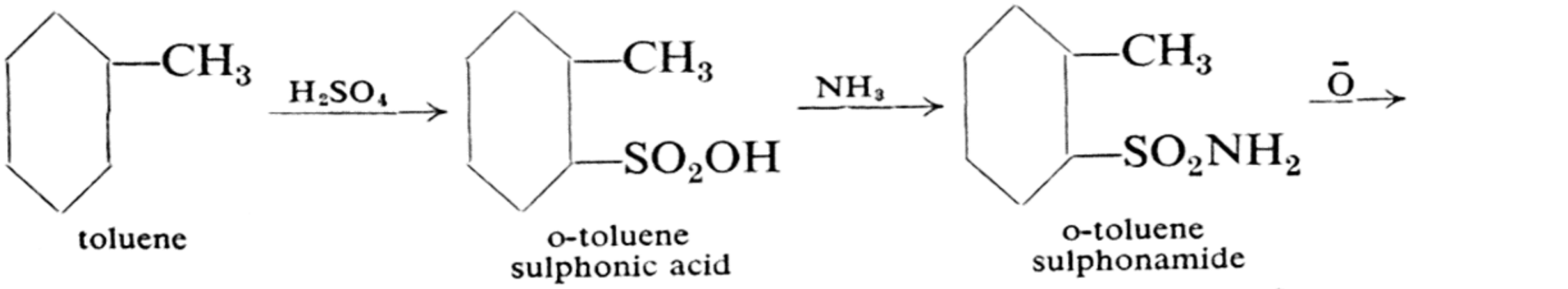
$$C_6H_5 . COCl + 2NH_3 \rightarrow C_6H_5 . CONH_2 + NH_4Cl$$

It is a colourless crystalline solid, m.p. 130°C. It may be purified by crystallization from hot water and is easily hydrolyzed, for example by boiling with aqueous NaOH, to form sodium benzoate and liberate ammonia.

Saccharin is o-benzoic-sulphonimide



and is prepared commercially by the following sequence of reactions—



toluene

o-toluene sulphonic acid

o-toluene sulphonamide

o-benzoic sulphonamide

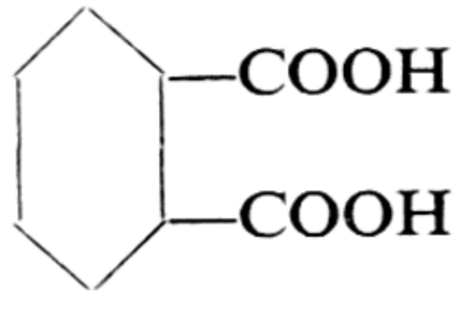
saccharin

Phenyl Acetic Acid, $C_6H_5 . CH_2COOH$, is obtained by the following reaction—

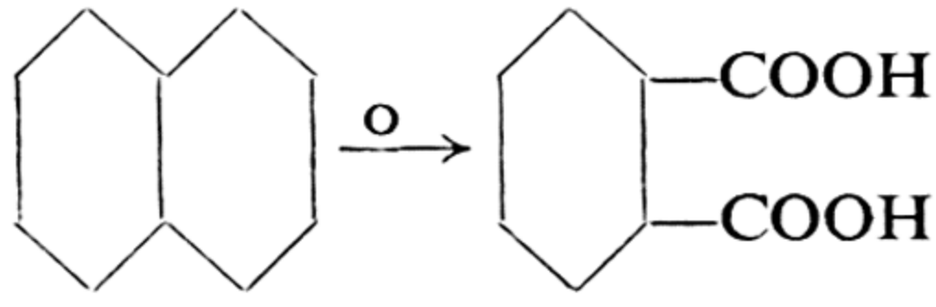
$$C_6H_5 . CH_2Cl \xrightarrow{KCN} C_6H_5 . CH_2CN \xrightarrow{H_2O} C_6H_5 . CH_2 . COOH$$

Cinnamic Acid, $C_6H_5 . CH{=}CH . COOH$. See Perkin's synthesis on page 1001.

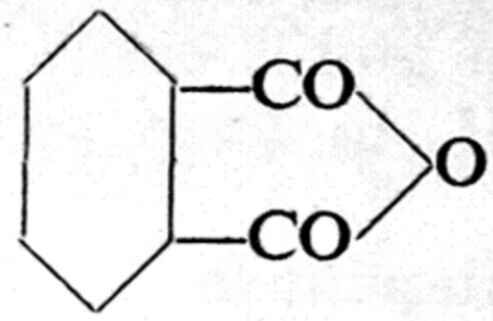
Phthalic Acid,



is prepared commercially by oxidizing naphthalene with fuming sulphuric acid in the presence of a small quantity of a mercury catalyst, or by vaporizing naphthalene in a stream of air and passing over a heated vanadium pentoxide catalyst—

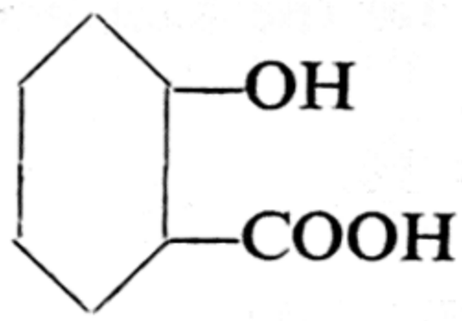


Phthalic anhydride,



may be prepared by heating phthalic acid. It is used extensively in the production of eosine and rhodamine dyes, and also as an intermediate in the manufacture of anthraquinone and hence of the important dye, alizarin.

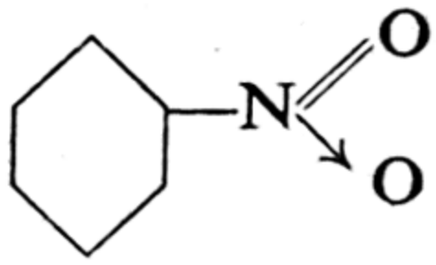
Salicylic Acid,



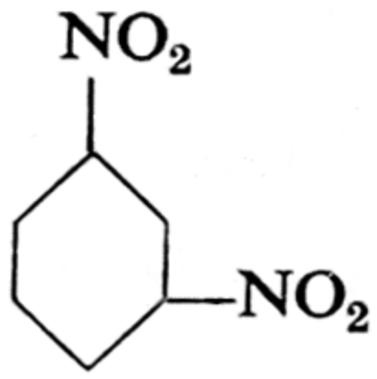
Sodium salicylate may be prepared from sodium phenate by the Kolbe's reaction (heat with CO_2—*see* p. 997). This is then converted into salicylic acid by treatment with mineral acids.

NITRO-COMPOUNDS

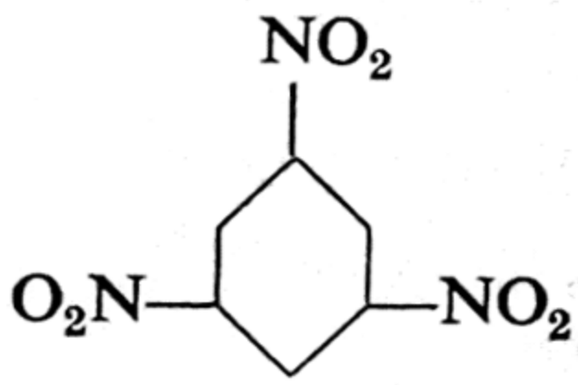
The aromatic nitro-compounds contain the univalent group —NO_2 linked directly to the benzene nucleus, e.g.



nitrobenzene

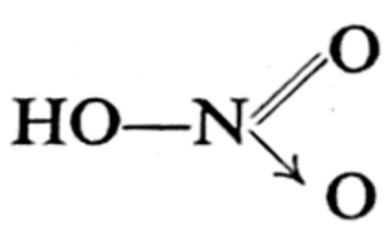


m-dinitrobenzene



1.3.5. trinitrobenzene

Nitrobenzene is prepared from benzene by the action of a mixture of concentrated nitric acid and concentrated sulphuric acid at ordinary temperatures. The function of the sulphuric acid appears to be to remove the water present in concentrated nitric acid (68 per cent HNO_3), so that the latter functions as



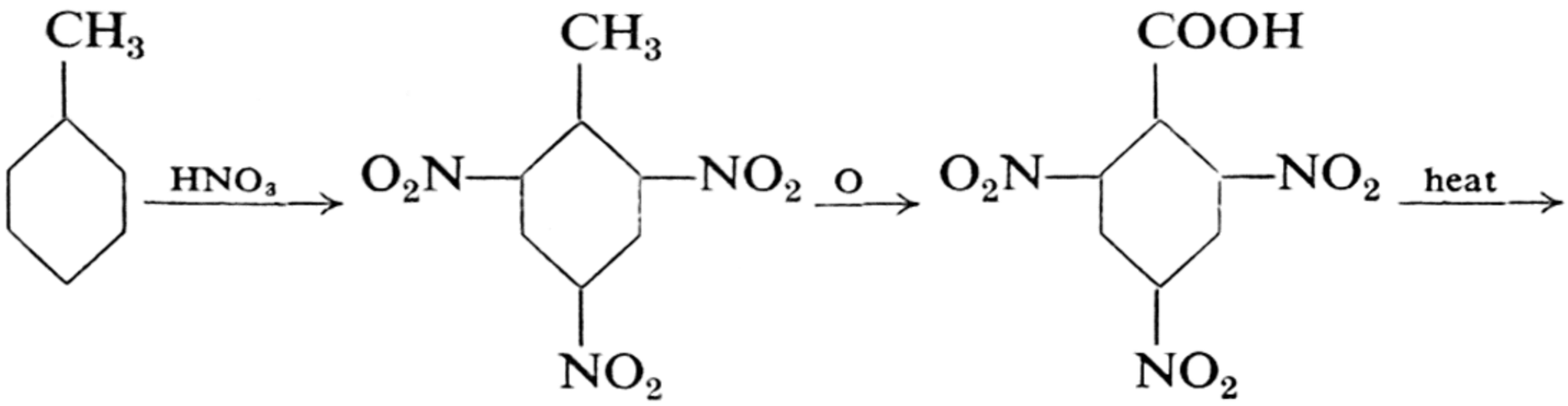
rather than as $H^+ + NO_3^-$ (but see also p. 665)

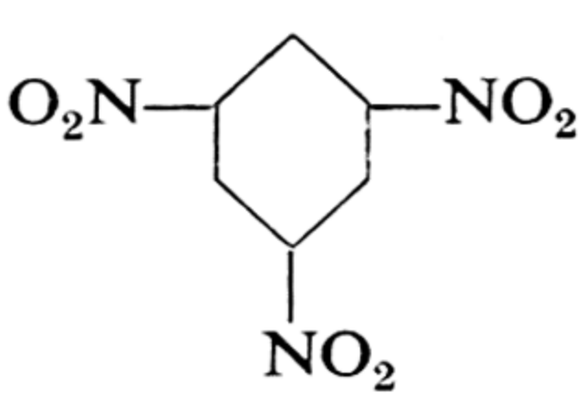
$$C_6H_5\boxed{H + HO-}NO_2 \rightarrow C_6H_5 . NO_2 + H_2O$$

Nitrobenzene is a pale yellow liquid, b.p. 210°C, with an almond-like odour which is often confused with that of benzaldehyde. It is used as a cheap scent in soaps, but its chief importance lies in its easy conversion to aniline, $C_6H_5 . NH_2$.

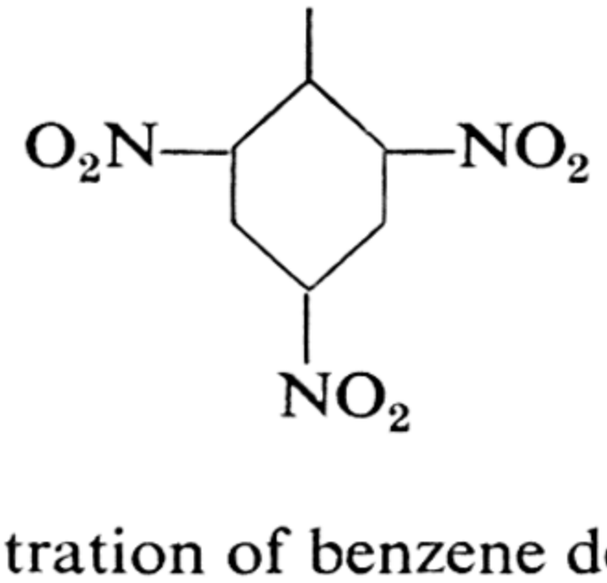
Meta-dinitrobenzene is prepared by the action of a mixture of fuming nitric acid and concentrated sulphuric acid on benzene or nitrobenzene in the hot. On subsequently pouring into water, the m-dinitrobenzene separates as a yellow solid, m.p. 90°C.

Trinitrobenzene is only prepared with difficulty by the action of fuming nitric acid and concentrated sulphuric acid on dinitrobenzene. It may, however, be prepared easily by nitrating toluene to give trinitro-toluene. The latter on oxidation is converted to trinitro-benzoic acid, which decomposes on warming to give trinitrobenzene.



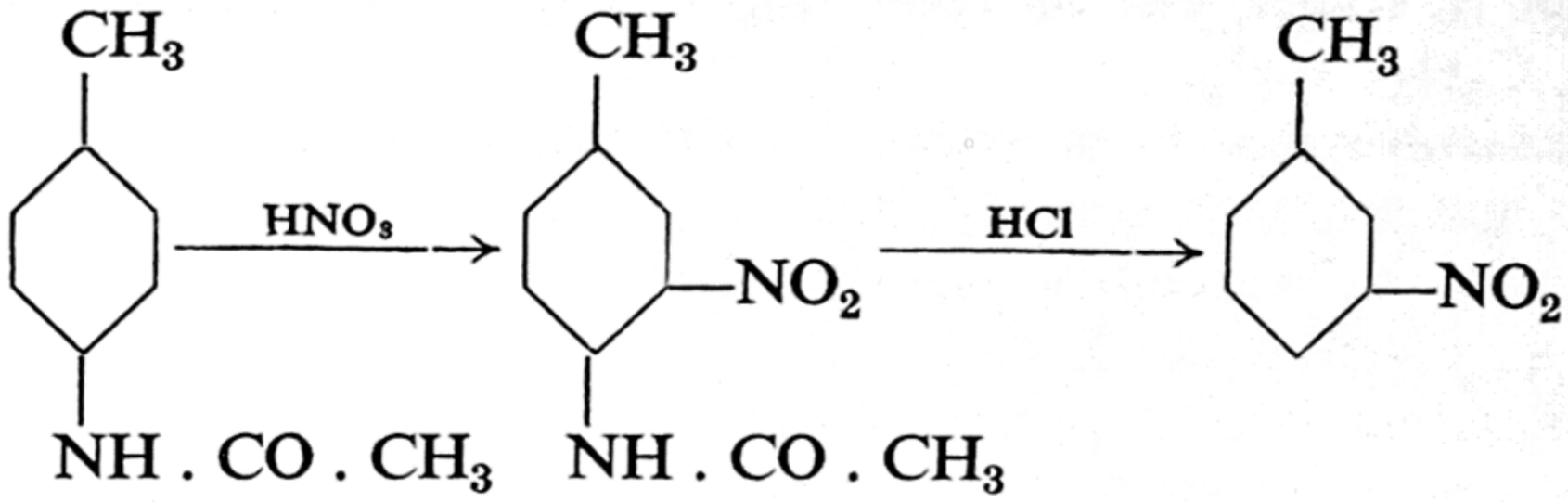


Phenol may easily be nitrated by dilute nitric acid in the cold to give a mixture of o- and p-nitrophenol. Further nitration occurs easily to give dinitro-phenol and trinitro-phenol (picric acid)



Note the relative ease of nitration of benzene derivatives which contain an ortho-para directing substituent. The methyl group in toluene, however, does not activate the benzene to anything like the extent of the —OH group in phenol, but nitro-derivatives are formed much more easily than with

benzene. This lower reactivity of the methyl group is illustrated by the following method for preparing meta-nitro toluene—



In this preparation the acetamide group is more strongly ortho-para directing than the methyl group, so that the entering nitro-group takes up the position ortho to the —NH . CO . CH_3 group (and meta to the —CH_3 group).

Properties. Aromatic nitro-compounds are usually pale-yellow substances, insoluble in and heavier than water, but mostly readily soluble in alcohol, ether and glacial acetic acid. Many explode when heated or on detonation, for example, trinitro-toluene ("T.N.T.") and trinitro-phenol (picric acid), but the lower members are volatile in steam and are usually separated by steam-distillation.

Reduction Compounds. The products obtained by the reduction of nitro-benzene vary with the conditions as follows—

1. Reduction in acid solution, for example, using tin and concentrated hydrochloric acid, gives aniline—

$$C_6H_5 . NO_2 \rightarrow \underset{\text{aniline}}{C_6H_5 . NH_2}$$

2. Reduction in neutral solution containing a little ammonium chloride as catalyst gives phenyl-hydroxylamine—

$$C_6H_5 . NO_2 \xrightarrow{\text{Zn dust}} C_6H_5 . NHOH$$

3. Reduction in alkaline solution gives such compounds as—

$$\underset{\text{azoxybenzene}}{C_6H_5—N(\rightarrow O)—N} \rightarrow \underset{\text{azobenzene}}{C_6H_5—N=N—C_6H_5} \rightarrow \underset{\text{hydrazobenzene}}{C_6H_5—NH—NH—C_6H_5}$$

Azoxybenzene may be prepared by reducing nitrobenzene with sodium methoxide in methyl alcohol solution.

Azobenzene is less easily prepared from nitrobenzene, but may be obtained fairly easily by heating azoxybenzene with iron filings.

Hydrazobenzene may be prepared by reducing nitrobenzene with zinc and sodium hydroxide in alcoholic solution. The hydrazobenzene dissolves in the alcohol and may subsequently be separated.

Nitrosobenzene, $C_6H_5 . NO$, is probably also formed during the reduction of nitrobenzene in alkaline solution, but as it is very easily further reduced to phenyl hydroxylamine and to aniline, it is not prepared by this method. Azoxybenzene produced as above, probably results from the reaction of the first formed nitrosobenzene with phenylhydroxylamine.

AROMATIC AMINES

The aromatic amines may be regarded as ammonia derivatives in which the hydrogen atoms are replaced by benzene or substituted benzene groups. They show a close resemblance to aliphatic amines both in the methods of preparation and in their properties. The phenyl group will of course

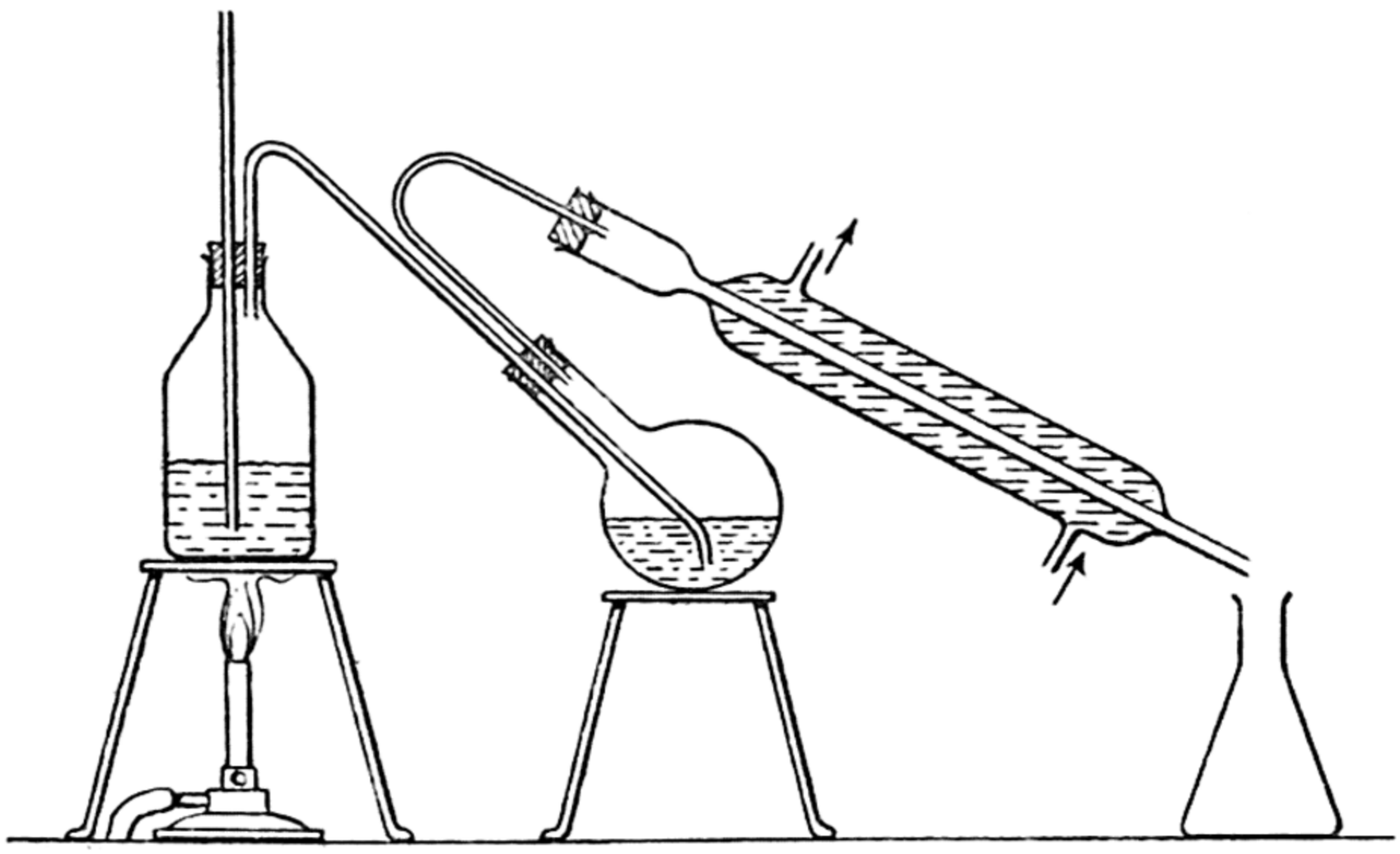


FIG. 270. Apparatus for Steam-distillation

tend to modify these properties. Thus the phenyl group has an "acidic" role in many of its compounds, so that the basicity of the aromatic amines decreases with increase in the number of phenyl groups. It will be recalled that with the purely aliphatic amines the reverse is the case and the basicity increases in the order primary, secondary, tertiary and quaternary. No purely aromatic quaternary amines are known, and of the primary, secondary and tertiary, the primary amines are especially important.

Aniline, $C_6H_5 . NH_2$, is the most important of the primary aromatic amines.

1. It may be prepared by the reduction of nitrobenzene in acid solution. The usual laboratory method uses tin and concentrated hydrochloric acid as the reducing agent.

$$C_6H_5 . NO_2 \xrightarrow{H} \underset{\text{aniline}}{C_6H_5 . NH_2}$$

About 25 g of nitrobenzene and 50 g of granulated tin are placed in a

large flask fitted with a reflux water-condenser. About 20 ml of concentrated hydrochloric acid are then added via the condenser and the mixture gently shaken. When the reaction slackens (moderate the reaction by immersing the flask in cold water from time to time), a further 20 ml of hydrochloric acid are added, and the process repeated until about 100 ml of the acid have been added. The reduction is then completed by heating the flask (without the condenser) for about 30 min on a water bath. The aniline is now present as the chlorostannate, $(C_6H_5 . NH_3)_2SnCl_6$. Treatment with excess of sodium hydroxide solution liberates the aniline as a dark-coloured oil, which is then separated by steam-distillation.

2. Aniline may also be prepared from benzamide by the Hofmann reaction (*see* p. 951)—

$$C_6H_5 . CONH_2(+ Br_2 + KOH) \rightarrow C_6H_5 . NH_2$$

3. By heating phenol with ammonia in the presence of zinc chloride at about 300°C, aniline is obtained—

$$C_6H_5OH + NH_3 \rightarrow C_6H_5NH_2 + H_2O$$

Commercially, aniline is prepared from nitrobenzene by the first method using iron filings instead of the more expensive granulated tin.

Properties. Aniline when freshly prepared is a colourless liquid, b.p. 184°C, but on exposure to air and light it develops a deep brown colour, and may ultimately become black. It is only very slightly soluble in water, but dissolves in hydrochloric acid and in other acids due to the formation of soluble salts. Since aniline is only weakly basic, however, these soluble salts are all appreciably hydrolyzed in solution and so have a strong acid reaction. For the same reason the salt, aniline carbonate, is not formed. With a more concentrated hydrochloric acid, the salt, aniline hydrochloride, separates as a white solid—

$$C_6H_5 . NH_2 + HCl \rightarrow C_6H_5 . NH_2 . HCl \text{ or } [C_6H_5 . NH_3]Cl$$

The second of these two formulae is the correct one, but the name *aniline hydrochloride* is the one by which this compound is usually known. The formulae of other such salts include—

$[C_6H_5 . NH_3]_2SO_4$, aniline sulphate or phenyl ammonium sulphate,

$[C_6H_5 . NH_3]NO_3$, aniline nitrate or phenyl ammonium nitrate.

Aniline forms sparingly soluble salts with chloroplatinic acid and also with hydrochloric acid solutions of gold chloride and of copper chloride, namely $[C_6H_5 . NH_3]_2PtCl_6$, $[C_6H_5 . NH_3]AuCl_4$, $[C_6H_5 . NH_3]CuCl_4$.

The following are typical aniline reactions.

(i) It reacts with metallic potassium or sodium giving compounds such as $C_6H_5 . NHK$ and $C_6H_5 . NK_2$, which are immediately decomposed by

water. These compounds react with bromobenzene, C_6H_5Br, to give secondary and tertiary aromatic amines, $(C_6H_5)_2NH$ and $(C_6H_5)_3N$.

(ii) It undergoes the Schotten-Baumann reaction with benzoyl chloride in the presence of sodium hydroxide to form benzanilide, $C_6H_5 . NH . CO . C_6H_5$.

(iii) Acetanilide, $C_6H_5 . NH . CO . CH_3$, is formed when aniline is treated with acetyl chloride or with acetic anhydride.

(iv) Aniline condenses with benzaldehyde when heated on a water bath—

$$C_6H_5 . NH_2 + OHC . C_6H_5 \rightarrow \underset{\text{benzylidene aniline}}{C_6H_5 . N{=}CH . C_6H_5}$$

With aliphatic aldehydes, compounds such as

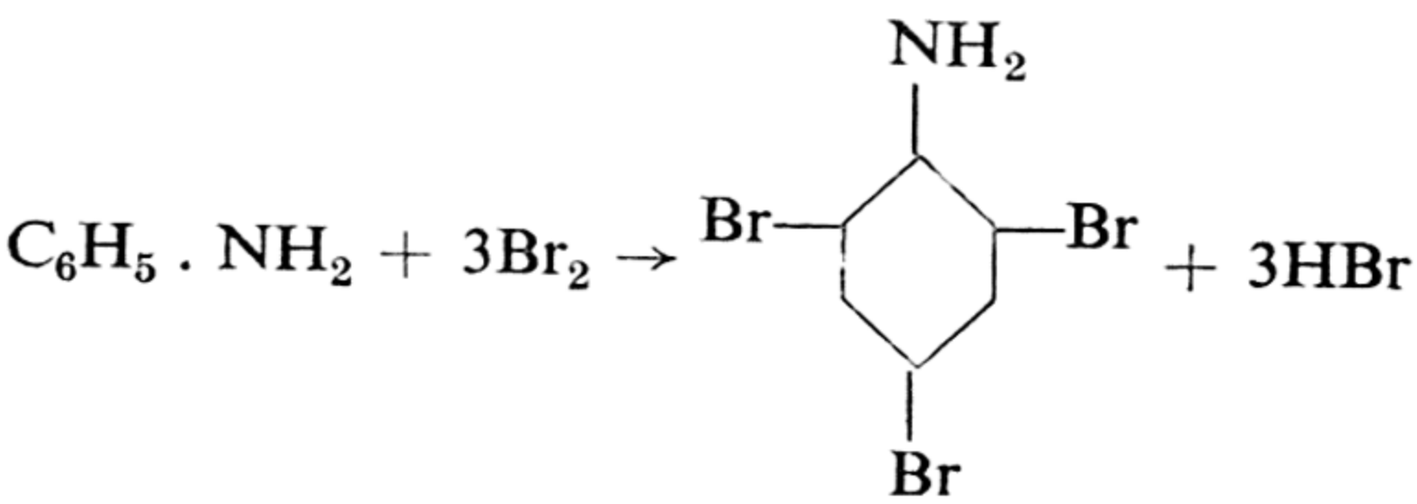
$$\begin{matrix} C_6H_5 . NH \\ \\ C_6H_5 . NH \end{matrix} \Big\rangle CH . CH_3$$

are formed.

(v) Aniline gives the usual carbylamine reaction for primary amines when warmed with chloroform and alcoholic potassium hydroxide—

$$C_6H_5 . NH_2 (+ CHCl_3 + KOH) \rightarrow \underset{\substack{\text{phenyl} \\ \text{carbylamine}}}{C_6H_5 . NC}$$

(vi) Aniline reacts readily with chlorine and with bromine. Thus, colourless crystals of tribromo-aniline are formed by drawing bromine vapour through an aqueous solution of aniline hydrochloride—



Similarly when aniline is shaken with bromine water, a white precipitate of the tri-bromide is formed. This reaction is of commercial importance for the recovery of bromine from weak aqueous solutions.

(vii) When aniline is treated in the cold with nitrous acid, the very important *diazo-compounds* are formed. These are discussed in detail in the next section.

$$C_6H_5 . NH_2 + O{=}NOH (+ HCl) \rightarrow [C_6H_5 . N{\equiv}N]Cl$$

When the solution is heated the diazonium compound decomposes—

$$C_6H_5 . N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

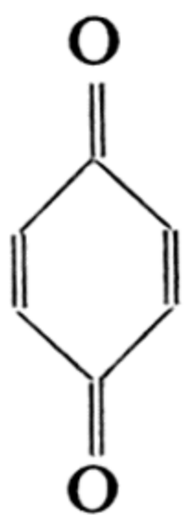
Primary aliphatic amines also react with nitrous acid, but the intermediate diazo-compounds are not formed and the reaction goes directly to the formation of the alcohol and liberation of nitrogen—

$$CH_3 . NH_2 + HNO_2 \rightarrow CH_3OH + N_2 + H_2O$$

(viii) Aniline is easily oxidized, but the product depends both on the nature of the oxidizing agent and on the conditions. Thus—

(*a*) Bleaching powder (or sodium hypochlorite solution) oxidizes aniline to a violet-coloured product. This reaction is sometimes used as a test for aniline—Runge's test.

(*b*) Acidified potassium dichromate oxidizes aniline to benzoquinone, $C_6H_4O_2$, known also as *quinone*



(*c*) Further oxidation produces a black dye-stuff with a very complex structure, known as *aniline black*.

Secondary and Tertiary Aromatic Amines, $(C_6H_5)_2NH$, diphenylamine, and $(C_6H_5)_3N$, triphenylamine. These are not particularly important. Diphenylamine is an extremely weak base, but it does react with nitrous acid to form a nitrosamine

$$(C_6H_5)_2NH + HO—NO \rightarrow (C_6H_5)_2N—NO$$

and may also be converted into the acetyl derivative $(C_6H_5)_2N—CO . CH_3$. Triphenylamine is even less important and is not even basic.

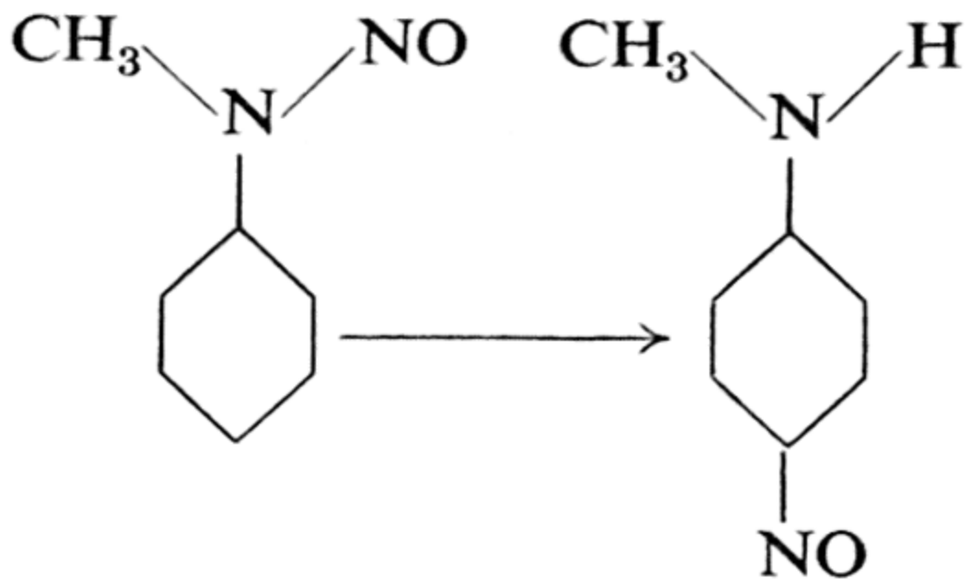
The mixed aliphatic-aromatic secondary and tertiary amines are much more important.

Methylaniline, $C_6H_5 . NH . CH_3$, is prepared, together with dimethyl aniline, by heating aniline with methyl iodide in a sealed tube under pressure.

The two compounds may be separated by converting methyl aniline into its acetyl derivative, and then distilling off the unchanged dimethyl aniline. The methyl aniline may then be obtained from the methyl acetanilide residue by hydrolysis and distillation.

Methyl aniline is more basic than aniline, and undergoes the usual reactions of secondary amines. The nitrosamine which it forms by reaction

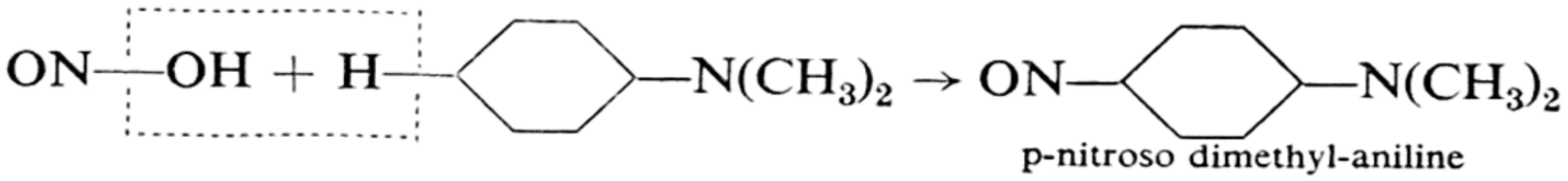
with nitrous acid isomerizes when allowed to stand in alcoholic HCl solution to form para-nitroso-methylaniline—



Since p-nitroso-methyl aniline is a base, it usually separates from the solution as the hydrochloride, but the free base may be liberated by subsequent treatment with aqueous sodium carbonate.

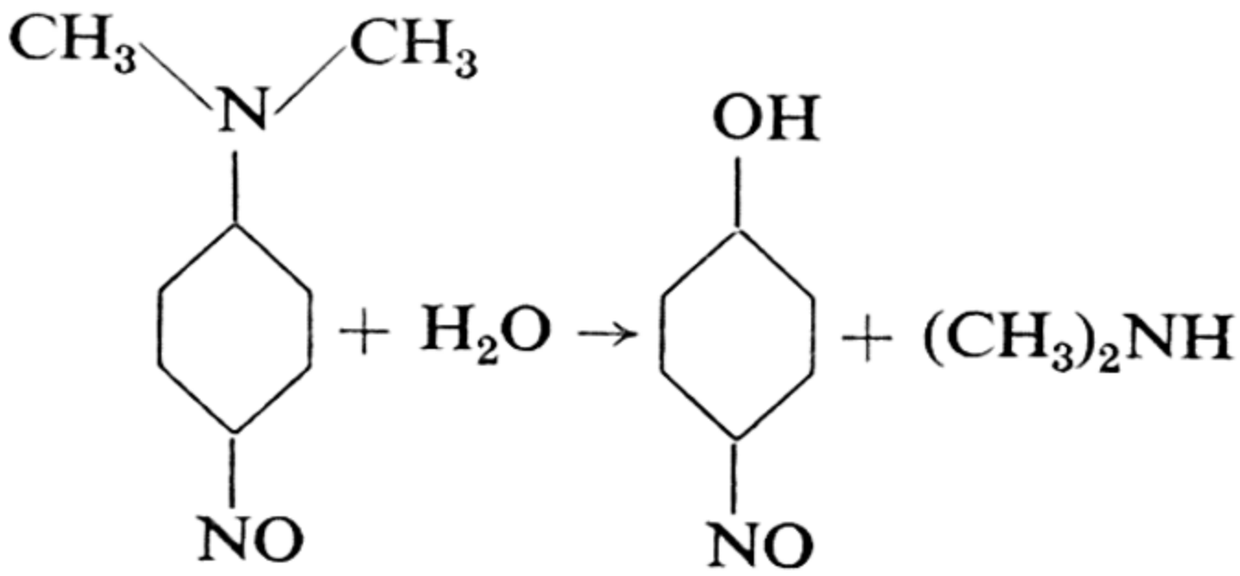
Dimethyl-aniline, $C_6H_5 . N(CH_3)_2$, is particularly important because of the various addition reactions which can occur at the para-position of the benzene ring. The di-methyl amino substituent appears to impart a very high degree of reactivity to the para-hydrogen atom of the benzene ring. This reactivity is illustrated by the following addition reactions—

(*a*) With *nitrous acid*, note that purely aliphatic tertiary amines do not react—

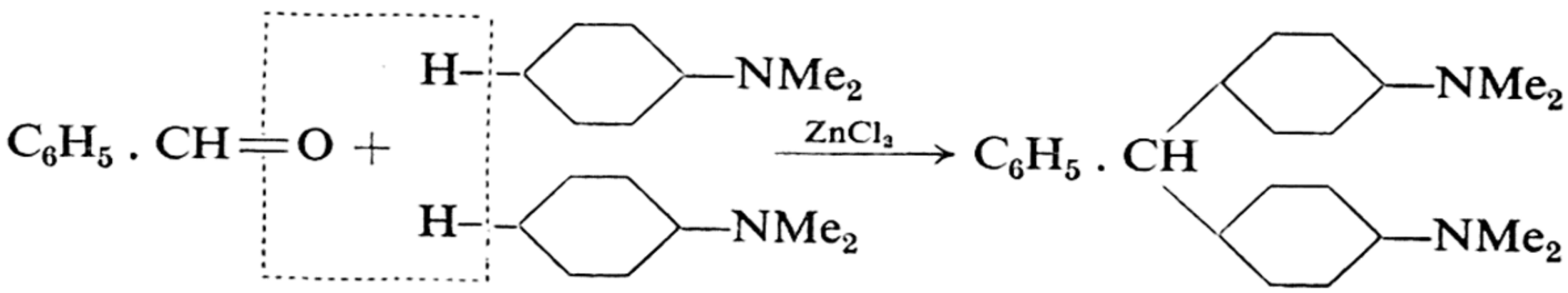


p-nitroso dimethyl-aniline

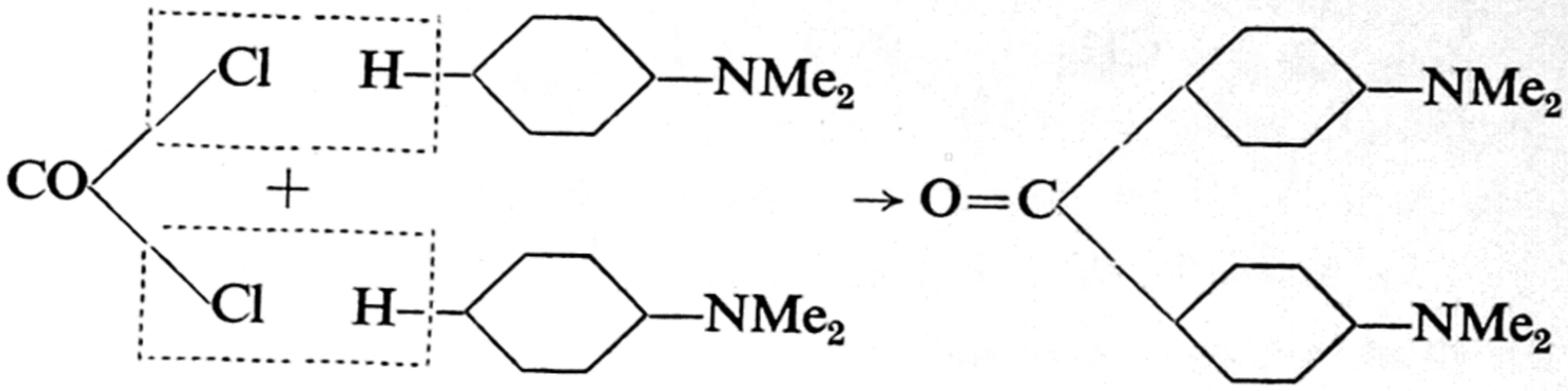
If the reaction is carried out by the action of a nitrite and hydrochloric acid, the nitroso-dimethyl aniline separates out as the hydrochloride, a yellow solid. This latter when hydrolyzed with aqueous sodium hydroxide gives p-nitroso phenol and the secondary amine, dimethylamine—



(*b*) With *benzaldehyde*, reaction occurs to give the base of Malachite Green—



(*c*) With *carbonyl chloride* (phosgene) the compound known as Mischler's ketone is formed—



DIAZONIUM COMPOUNDS

The important diazonium compounds were discovered by Griess in 1860. They are prepared by the action of cold nitrous acid and a mineral acid, such as hydrochloric acid, on an aromatic primary amine—

$$C_6H_5 . NH_2 + HCl + HNO_2 \rightarrow C_6H_5 . N_2 . Cl + 2H_2O$$

This type of reaction is known as the *diazo reaction*, and the compounds were originally known as diazo-compounds. The term diazonium compound however, is nowadays preferred because of the general similarity in properties which these compounds show to ammonium compounds, and they are formulated as—

$$[C_6H_5—N\equiv N]Cl \quad \text{or} \quad C_6H_5—\overset{\overset{|||}{N}}{N^+}\}Cl^-$$

Diazo-compounds are also known; these are formulated as

$$C_6H_5—N=N—Cl$$

Their properties, however, are different from those of the true diazonium compounds.

Preparation of Benzene Diazonium Chloride. An aqueous solution of benzene diazonium chloride is prepared from aniline by the following diazo reaction. The aniline is dissolved in a slight excess of dilute hydrochloric acid (1 : 2·2 molecular equivalents) and the solution cooled to about 5°C by immersing the flask in a suitable freezing mixture. Slightly more than the calculated quantity of a solution of sodium nitrite is then added drop-wise over a period of time. During this addition, the contents of the flask are kept well stirred, preferably by a mechanical stirrer, and the temperature of the reacting mixture maintained at about 5°C. If the temperature is allowed to increase the diazonium chloride decomposes to form phenol; if, on the other hand the temperature is reduced to about 0°C the rate of diazotization becomes unnecessarily slow. The sodium nitrite solution should be added until there is a slight excess of free nitrous acid in the solution. This is indicated by spotting out portions of the reaction mixture on to starch-iodide paper. If the latter is immediately turned blue,

then excess of nitrous acid is present and the diazotization is complete. The resulting solution of benzene diazonium chloride may then be used directly to carry out the reactions described below.

The following experimental conditions for successful diazotization should be carefully noted—

(*a*) The temperature of the reaction mixture should not be greater than 10°C. At higher temperatures, the diazonium compound decomposes—

$$C_6H_5—N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

(*b*) The nitrous acid should be prepared in situ, and be sufficient to diazotize all the aniline. If insufficient sodium nitrite is added, the unchanged aniline will react with the diazonium chloride to form diazoaminobenzene—

$$C_6H_5—N_2\boxed{Cl + H}NH \cdot C_6H_5 \rightarrow C_6H_5—N_2—NH \cdot C_6H_5 + HCl$$

Properties. Diazonium compounds are usually very soluble in water, but are sparingly soluble in alcohol and in ether. They are neutral, strongly ionized, form sparingly soluble platinichlorides, and are clearly the salts of a very strong base. The latter may be prepared from the diazonium chloride by reaction with silver oxide. These properties all point to the ammonium-type of formula with the chlorine present as the negatively charged chloride ion.

$$\begin{matrix} C_6H_5—N^+ \\ \| \\ N \end{matrix}\Big\}Cl^-$$

When an aqueous solution of benzene diazonium chloride is added to a cold concentrated solution of potassium hydroxide, the unstable potassium diazotate is formed. This diazo-compound changes to the more stable, isomeric iso-diazotate on heating with alkali to about 130°C. These two compounds are not diazonium compounds. They are called diazo-compounds and are considered to have the following formulae, in which the two compounds show geometrical isomerism comparable to that shown by fumaric and maleic acids (*see* p. 974)—

$$\begin{matrix} C_6H_5—N \\ \| \\ KO—N \end{matrix} \rightarrow \begin{matrix} C_6H_5—N \\ \| \\ N—OK \end{matrix}$$

Reactions of Diazonium Compounds

A. Reactions in which nitrogen is liberated

(i) Formation of phenol on warming the aqueous solution—

$$C_6H_5—N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

Note that nitrous acid converts *aliphatic* primary amines directly to the alcohols.

(ii) *Sandmeyer's Reaction*

$$C_6H_5—N_2Cl + Cu_2Cl_2 \rightarrow C_6H_5—Cl + N_2$$
$$C_6H_5—N_2Cl + Cu_2Br_2 \rightarrow C_6H_5—Br + N_2$$
$$C_6H_5—N_2Cl + Cu_2(CN)_2 \rightarrow C_6H_5—CN + N_2$$

The reaction is carried out by warming the solution of the diazonium chloride with the appropriate cuprous salt. In the case of the chloride, a solution of cuprous chloride in hydrochloric acid is used; for the bromide the solution is cuprous bromide in hydrobromic acid, whilst for the cyanide, a solution of potassium cuprocyanide is used.

(iii) Chlorobenzene may also be prepared by *Gattermann's method* which consists in treating the solution of benzene diazonium chloride with finely divided copper powder. The latter acts catalytically even at room temperature to form chlorobenzene with evolution of nitrogen—

$$C_6H_5—N_2Cl \rightarrow C_6H_5—Cl + N_2$$

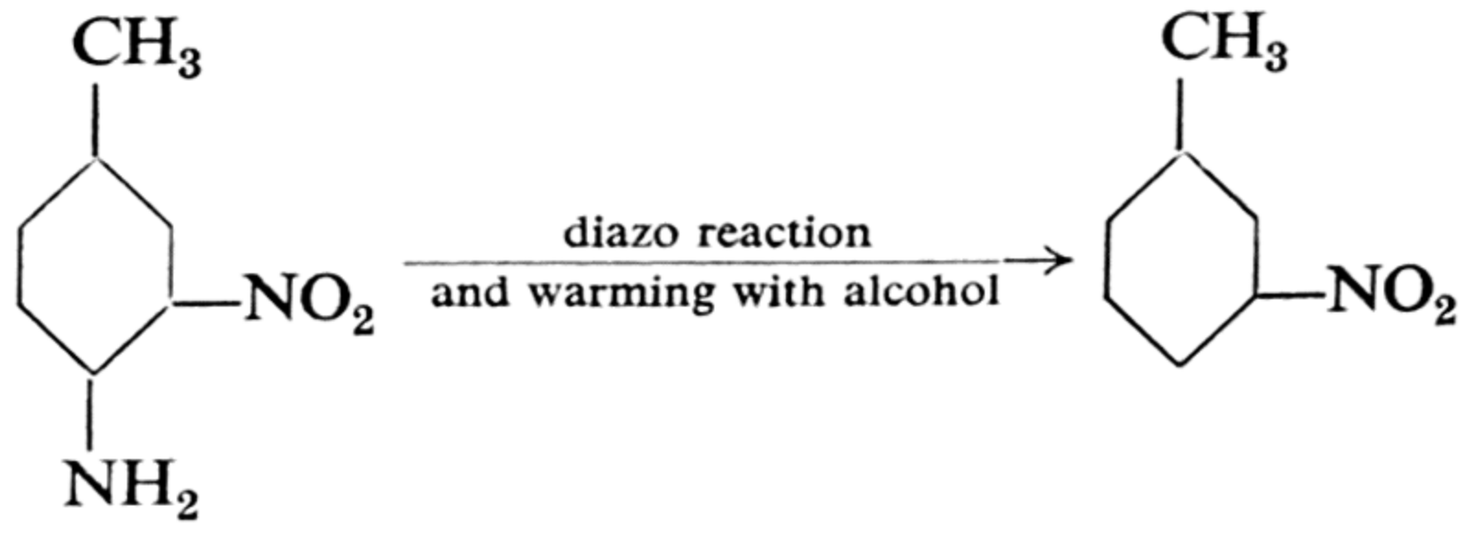
(iv) It is not necessary to use a copper catalyst to prepare iodobenzene. If the solution of the diazonium chloride is treated in the cold with a solution of potassium iodide, the resulting diazonium iodide decomposes readily to form iodobenzene—

$$C_6H_5—N_2Cl \xrightarrow{KI} C_6H_5—N_2I \xrightarrow{heat} C_6H_5—I + N_2$$

(v) If the diazotization is carried out in presence of alcohol, then on warming, either of the following reactions may occur—

$$C_6H_5—N_2Cl + C_2H_5OH \rightarrow C_6H_6 + N_2 + CH_3 . CHO + HCl$$
$$C_6H_5—N_2Cl + C_2H_5OH \rightarrow C_6H_5—OC_2H_5 + N_2 + HCl$$

The nature of the product is largely determined by the nature of the original primary amine. The former reaction tends to occur most easily the more acidic the original amines, e.g.



(vi) The $—N_2Cl$ group may also be replaced by H by reducing the diazonium chloride with stannous chloride in sodium hydroxide solution—

$$C_6H_5—N_2Cl(+ Na_2SnO_2) \rightarrow C_6H_6 + N_2 + \text{etc.}$$

(vii) Diazonium benzene chloride may be converted into nitrobenzene

by treatment with a nitrite in the presence of cupric oxide and copper as catalyst—

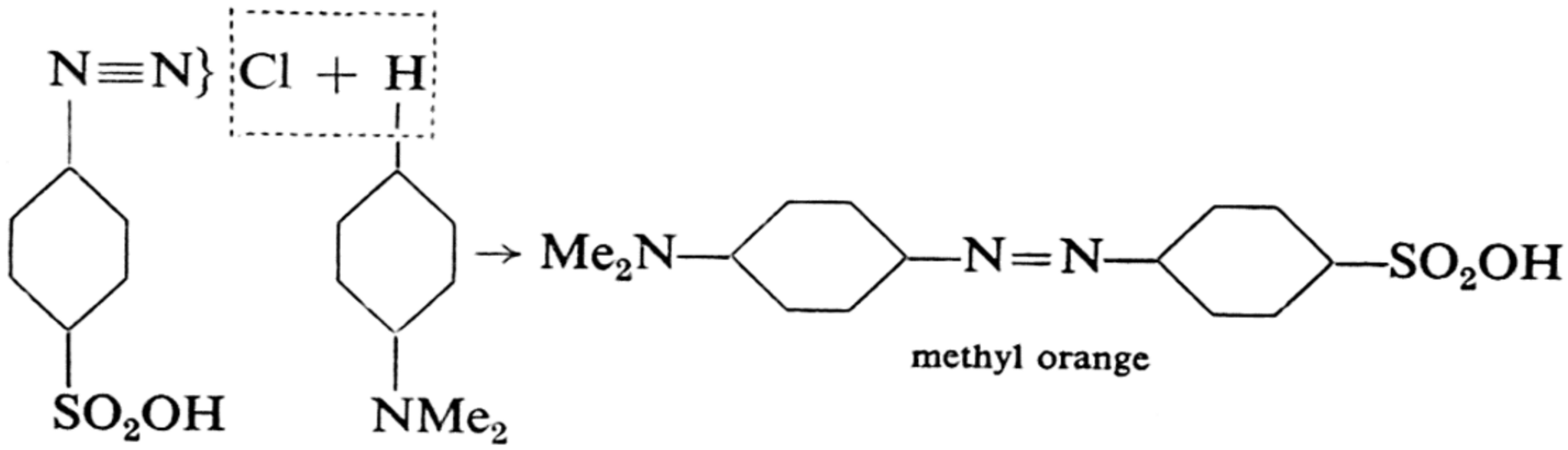
$$C_6H_5 . N_2Cl + KNO_2 \rightarrow C_6H_5NO_2 + KCl + N_2$$

B. Addition reactions in which nitrogen is not liberated

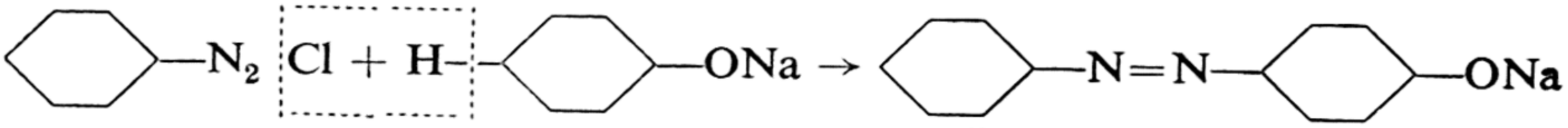
(i) Reduction of benzene diazonium chloride by stannous chloride in hydrochloric acid solution gives phenyl hydrazine hydrochloride—

$$C_6H_5—N_2Cl + 4\overline{H} \rightarrow C_6H_5—NH—NH_2 + HCl$$

(ii) *Coupling Reactions.* The following coupling reactions are very important in the formation of the so-called azo-dyes. The coupling reaction occurs preferably at the para-position, or if this is already occupied, in the ortho-position—



methyl orange



sodium p-hydroxy azobenzene

DYES

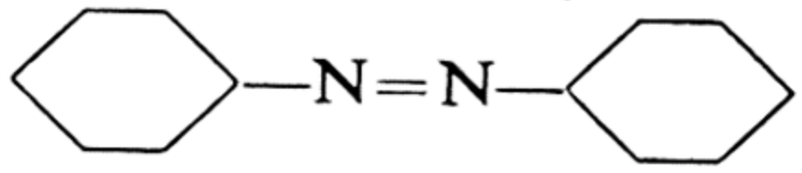
These are organic compounds of various structures which are characterized by the presence in their molecules of a *chromogen* and an *auxochrome*, as expressed by the general equation—

$$\text{DYE} = \text{CHROMOGEN} + \text{AUXOCHROME}$$

The chromogen is an aromatic compound which possesses a group known as a *chromophore*, the more important of which are

$$—N=N—, \quad >C=O, \quad >C=S, \quad \geqslant C—S—S—C\leqslant, \quad —NO, \quad —NO_2$$

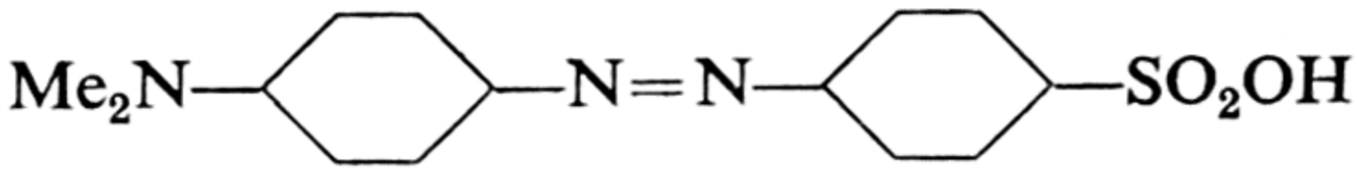
These groups impart colour to an aromatic molecule, but by themselves are insufficient to make the resulting compound a dye. Thus azobenzene



although it possesses a brilliant red colour, is not a dye. To become a dye, some other group is necessary to enable the resulting compound to adhere or become fixed to a textile fibre. Such groups are known as *auxochromes*, and include salt-forming groups such as —OH, $—NH_2$, or their derivatives, and also such groups as $—SO_2OH$ and —COOH which impart solubility to the dye.

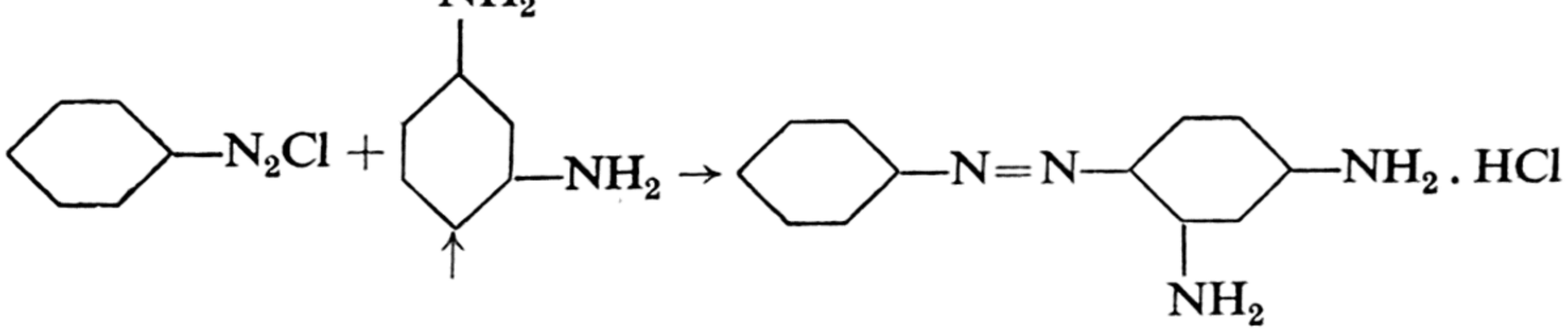
More than a half of all the dyes used commercially are azo-dyes and are produced by the reactions above, i.e. diazotization followed by a coupling reaction in the presence of dilute acid or alkali. The simpler azo-dyes are yellow, but by varying the auxochrome and increasing the number of carbon atoms in the aromatic portion of the molecule, the colour deepens and all the colours of the spectrum may be produced. In general the azo-dyes are produced by adding the solution of the diazonium compound to the aromatic amine, phenol, naphthol, or derivatives of these. The coupling occurs preferentially in the para-position to the hydroxyl or amino group, but if this is already occupied coupling may occur in the ortho-position. If neither of these positions is vacant, then coupling does not occur. These reactions are exemplified by the following examples of the formation of azo-dyes—

(*a*) *Methyl Orange* (*see* above)



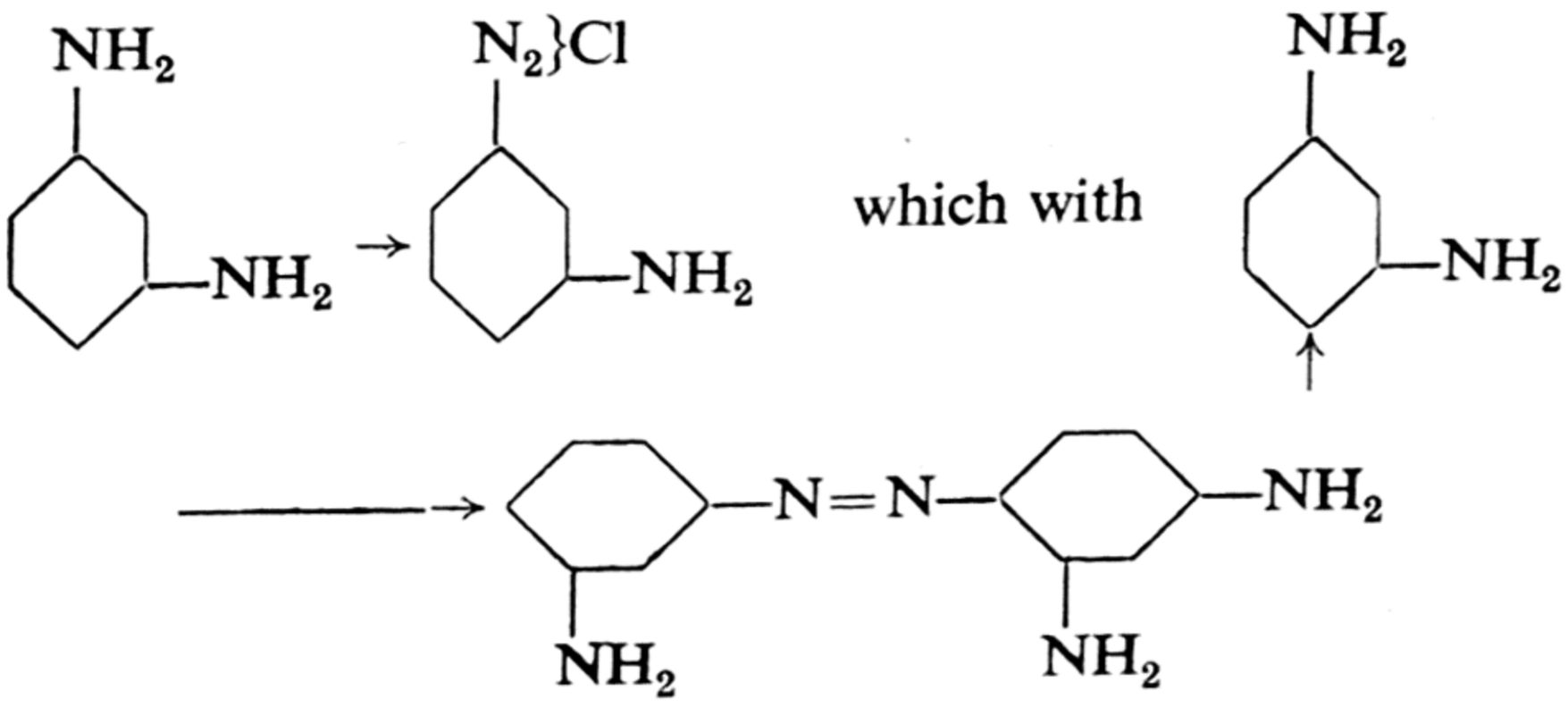
Formed by diazotizing sulphanilic acid and coupling with dimethyl-aniline.

(*b*) *Chrysoïdine Yellow*

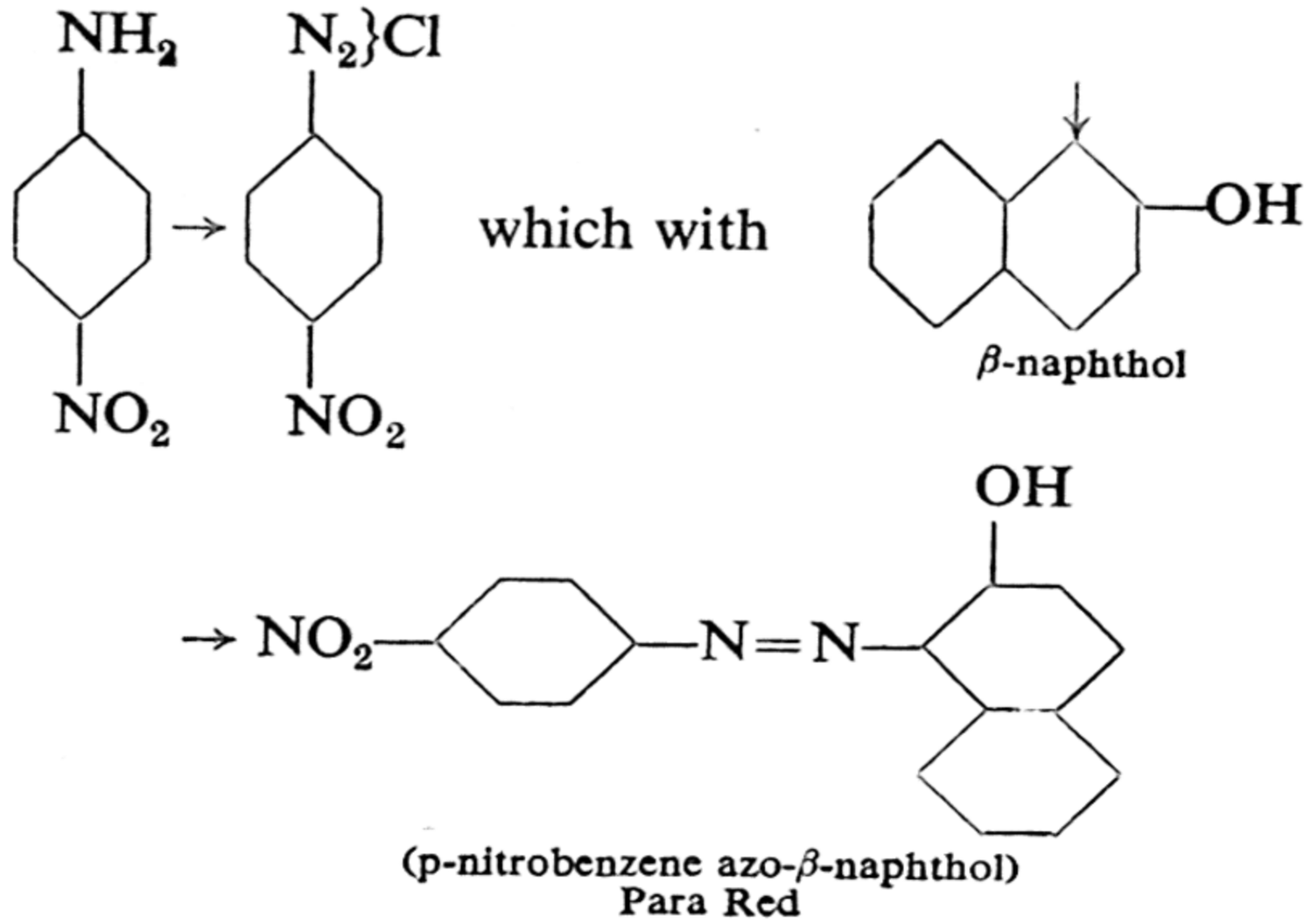


The m-phenylene diamine couples para- to one of the $-NH_2$ groups (and ortho- to the other). Chrysoïdine yellow dyes silk and wool directly with an orange-red colour.

(*c*) *Bismarck Brown.* When meta-phenylene diamine is diazotized it couples with itself to form Bismarck Brown, the formation of which is sometimes used as a very delicate test for nitrous acid—



(*d*) *Para Red.* This and other related dyestuffs are usually prepared directly in contact with the cloth fibre by impregnating the fabric with β-naphthol and immersing the prepared fabric into an aqueous solution of the diazotized amine, such as p-nitraniline.



(p-nitrobenzene azo-β-naphthol)
Para Red

CHAPTER 37

ANALYSIS OF ORGANIC COMPOUNDS

In the present chapter it is proposed to review the stages involved in determining the molecular formula of organic compounds. These stages are classified as follows—

(1) Preparation of the compound in a pure form.

(2) Qualitative analysis to determine the elements present in the pure compound. Thus aniline contains carbon, hydrogen and nitrogen.

(3) Determination of the relative proportion of these elements by weight. The results are usually expressed on a weight percentage basis. Thus, aniline is found to contain 77·42 per cent of carbon, 15·05 per cent of nitrogen and 7·53 per cent of hydrogen by weight.

(4) Determination of the Empirical Formula from the percentage composition. The empirical formula expresses the relative numbers of the different atoms present in the molecule of the substance.

(5) To obtain the molecular formula from the empirical formula it is next necessary to determine the molecular weight of the compound. Thus, the empirical formula of acetic acid is found to be CH_2O, but the molecular weight is double this, i.e. 60, so that the molecular formula of acetic acid must be $C_2H_4O_2$.

(6) The final stage in determining the structural formula of the organic compound is dependent on a knowledge of the chemical reactivity of that compound. Thus, aniline shows the reactions of a primary amine and therefore contains the group $—NH_2$. It also shows many of the reactions of benzene and may be converted into this compound, for example by diazotization followed by the Sandmeyer reaction. The formula of aniline appears therefore to be $C_6H_5 . NH_2$, and this formula is confirmed by the numerous other reactions of aniline.

Purification of the Organic Compound

The purification of an organic compound may be a relatively easy process but more often it is a somewhat difficult process, and the choice of the different methods available to effect the purification will vary from case to case. The more important of the simpler methods of purification may briefly be summarized as follows—

(*a*) Recrystallization of the substance, if a solid, from a suitable solvent. The solution is usually prepared in the hot, filtered and the filtrate allowed to crystallize. The mother liquor usually retains most of

the impurities, but sometimes it is necessary to recrystallize the substance again from fresh solvent.

(*b*) If the substance is a liquid, it may either be converted into a solid derivative and the latter purified by recrystallization, or it may be separated by the method of distillation. The variations of this latter method include fractional distillation, and also distillation under reduced pressure. The latter is usual in those cases where the substance would otherwise decompose at its boiling point under atmospheric pressure. Other distillation methods include steam-distillation (e.g. purification of aniline) and azeotropic distillation (e.g. preparation of anhydrous alcohol).

If the substance after purification has a sharp melting point or boiling point, then it may be taken to be pure. This follows from the fact that impurities tend to spread out the temperature of melting, although in some cases an indefinite melting point may result from decomposition of an otherwise pure compound.

Qualitative Analysis

Identification of Elements Present

Carbon and Hydrogen. If the substance is definitely organic the presence of carbon may be assumed and it is almost certain that hydrogen will also be present. If a direct test is required, the procedure is to mix a little of the powdered substance with about ten times its weight of perfectly dry cupric oxide in powder form, and heat the mixture in a dry tube as in the diagram. The carbon and hydrogen present in the compound are oxidized to carbon dioxide and steam respectively. The latter condenses on the upper portion of the tube, and the former is detected by passing through lime-water.

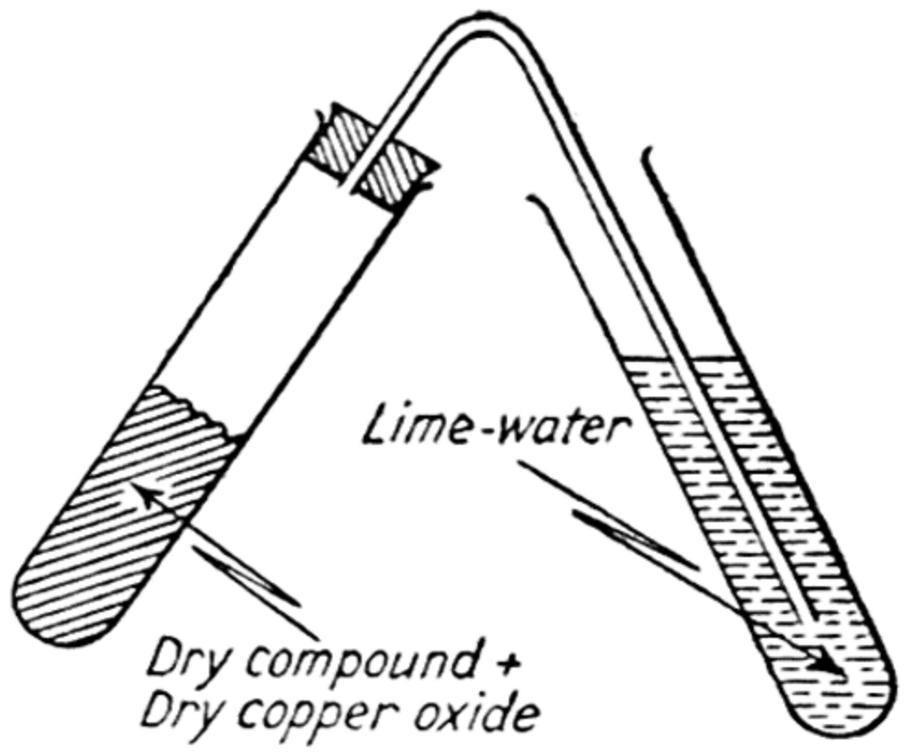


FIG. 271. Detection of Carbon and Hydrogen

Nitrogen. Some organic compounds containing nitrogen give off ammonia when heated alone or with soda-lime. A negative result, however does not necessarily indicate the absence of nitrogen, since there are many nitrogen-containing organic compounds, such as nitro-benzene, which fail to give this test. It is more usual, therefore, to carry out the following Lassaigne test, which is general for all organic compounds containing nitrogen and also for detecting the halogen elements and sulphur.

Lassaigne's Sodium-fusion Test. A small rimmed test-tube is supported vertically from a piece of asbestos cardboard resting on the ring of a retort stand, shown on p. 1022. A piece of clean sodium, about the size of a pea, is dropped into the test-tube and then carefully heated until it begins to melt and vaporize. At this stage, a small quantity of the dry organic

compound is added so that it falls directly on to the molten sodium (if the substance is liquid, it may be added via a dropping-tube). A vigorous reaction usually occurs—indeed, such substances as chloroform, carbon tetrachloride, explode in contact with sodium vapour and must not be submitted to this test. The test-tube is then heated strongly until the lower portion of the test-tube is red-hot, and at this stage it is plunged into an evaporating basin or small beaker containing distilled water. This operation should be carried out firmly and with due precautions since any residual sodium will explode in contact with the water. The charred mass in the evaporating basin is then ground up with the water and the solution filtered.

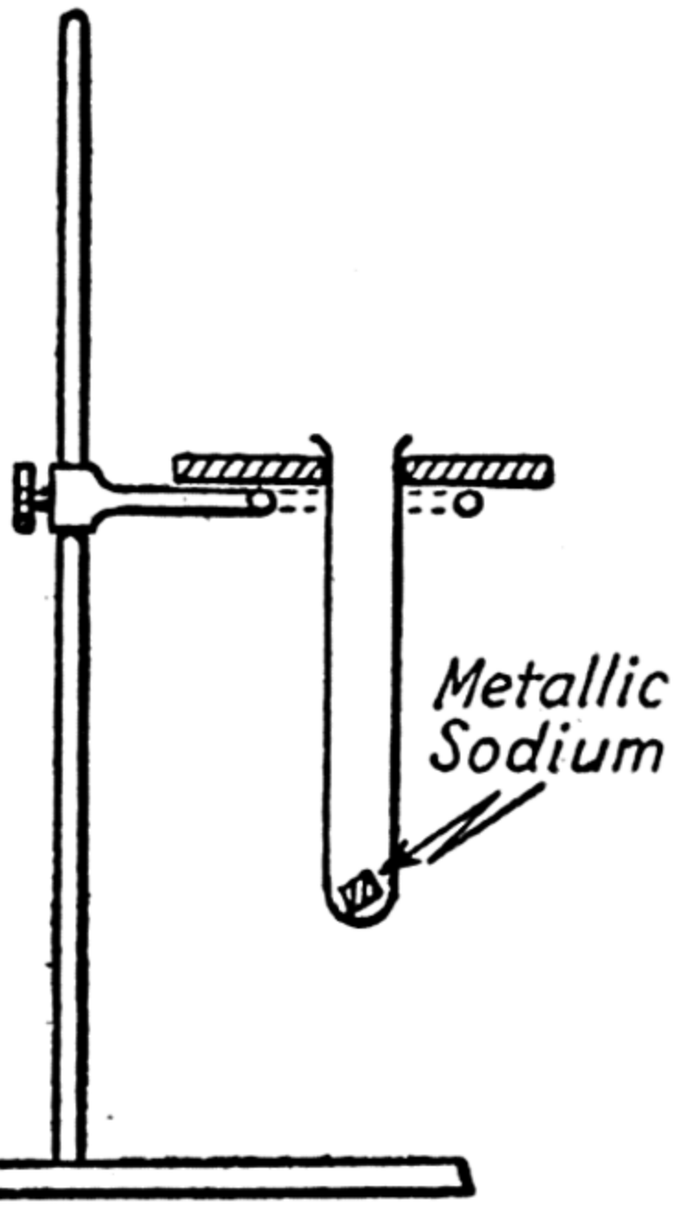


FIG. 272. Apparatus for Lassaigne Test

This solution will contain nitrogen (if present) as sodium cyanide, the halogens (if present) as the sodium halides and sulphur (if present) as sodium sulphide. The second part of the test thus involves the detection by the usual chemical reactions of (*a*) a cyanide, (*b*) a halide and (*c*) a sulphide. A portion of the filtrate is therefore tested for cyanide as follows. Ferrous sulphate solution and a little sodium hydroxide are added and the mixture boiled to convert the cyanide into the ferrocyanide—

$$6NaCN + FeSO_4 = Na_4[Fe(CN)_6] + Na_2SO_4$$

Two to three drops of a ferric chloride solution are then added to convert the ferrocyanide to the deep-blue ferric ferrocyanide (Prussian Blue). The solution is then cooled and acidified with concentrated hydrochloric acid to dissolve any ferrous and ferric hydroxides present. A blue solution or blue precipitate of Prussian Blue indicates the presence of nitrogen in the original organic compound. If the solution is coloured green, then nitrogen may be present and it is advisable to repeat the test.

$$3Na_4[Fe(CN)_6] + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12NaCl$$

Halogens. A second portion of the solution from the Lassaigne sodium-fusion test is boiled with nitric acid to expel HCN if nitrogen was found to be present (otherwise this nitric acid boiling may be omitted)—

$$NaCN + HNO_3 = NaNO_3 + HCN$$

Silver nitrate solution is then added. A curdy white precipitate indicates the presence of chlorine in the original substance; a cream or yellow precipitate similarly indicates bromine or iodine. The exact nature of the halogen is indicated by the usual methods of acid radical tests.

Beilstein's Test. This very rapid test is usually carried out before the sodium fusion test for the halogen. A piece of clean copper gauze is first oxidized by heating in the bunsen flame until the latter is no longer coloured green. A small quantity of the organic compound is then placed on the oxidized copper gauze and the heating continued. If the flame is coloured bright green, the presence of a halogen is indicated.

Sulphur. A third portion of the solution from the Lassaigne sodium-fusion test is treated with a freshly prepared solution of sodium nitroprusside. If the solution is coloured purple (resembling permanganate) the presence of sulphur in the original organic compound is indicated. Alternatively, the presence of sulphide in the solution from the sodium fusion test may be indicated by placing a little on a clean silver coin. If sulphur is present, the formation of black silver sulphide will be revealed by the blackening of the coin.

Metals. These are detected by strongly igniting the organic compound and examining the solid residue (if any) by the usual methods of qualitative analysis.

No general method for detecting and estimating oxygen in an organic compound is known.

Quantitative Analysis

Determination of Percentage Composition. Limitations of space prevent a full discussion with experimental details of the quantitative methods for estimating carbon, hydrogen, nitrogen, halogens and sulphur in an organic compound, but these details may be obtained if required from any book on practical organic chemistry. In the following account, only the general procedure in making these determinations is described.

Carbon and Hydrogen. The method is based on the qualitative method. A known weight of the organic compound is completely oxidized by heating in a current of pure dry oxygen and the resulting carbon dioxide (containing the whole of the carbon) and water (containing the whole of the hydrogen) are collected and weighed.

$$C_mH_n + \text{oxygen} \rightarrow mCO_2 + n/2\ H_2O$$

The water is absorbed in weighed calcium chloride tubes, and the carbon dioxide in weighed potash or soda-lime tubes. The essential parts of the apparatus are shown in the two diagrams on p. 1024.

Nitrogen. There are two general methods available. The first, Dumas' method, in which all the nitrogen present in the organic compound is liberated as nitrogen, the volume of which is measured; the second, Kjeldahl method, of less general application, converts the nitrogen into ammonia.

Dumas' Method. This is essentially a modification of the above method for determining carbon and hydrogen. The compound is heated in a

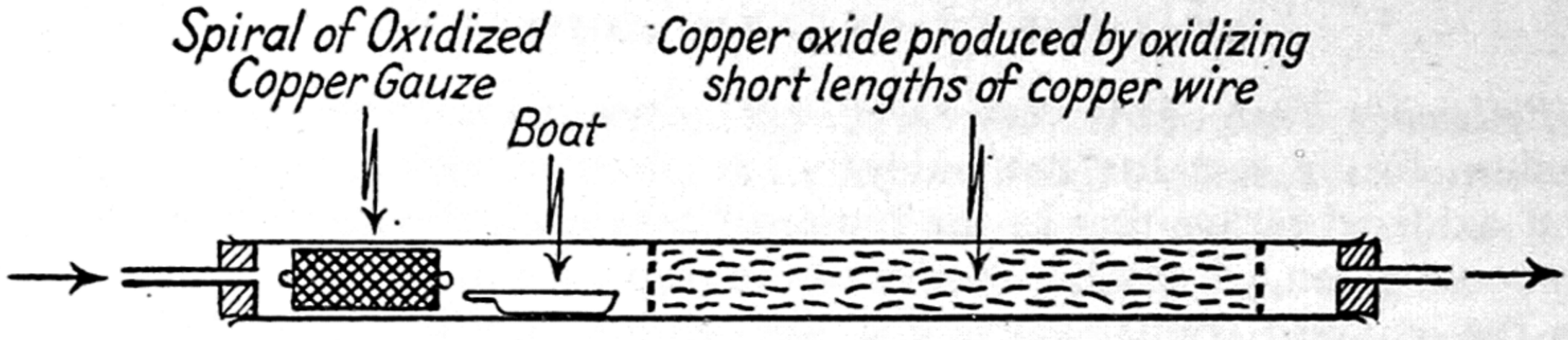


FIG. 273. Combustion Tube for Carbon and Hydrogen

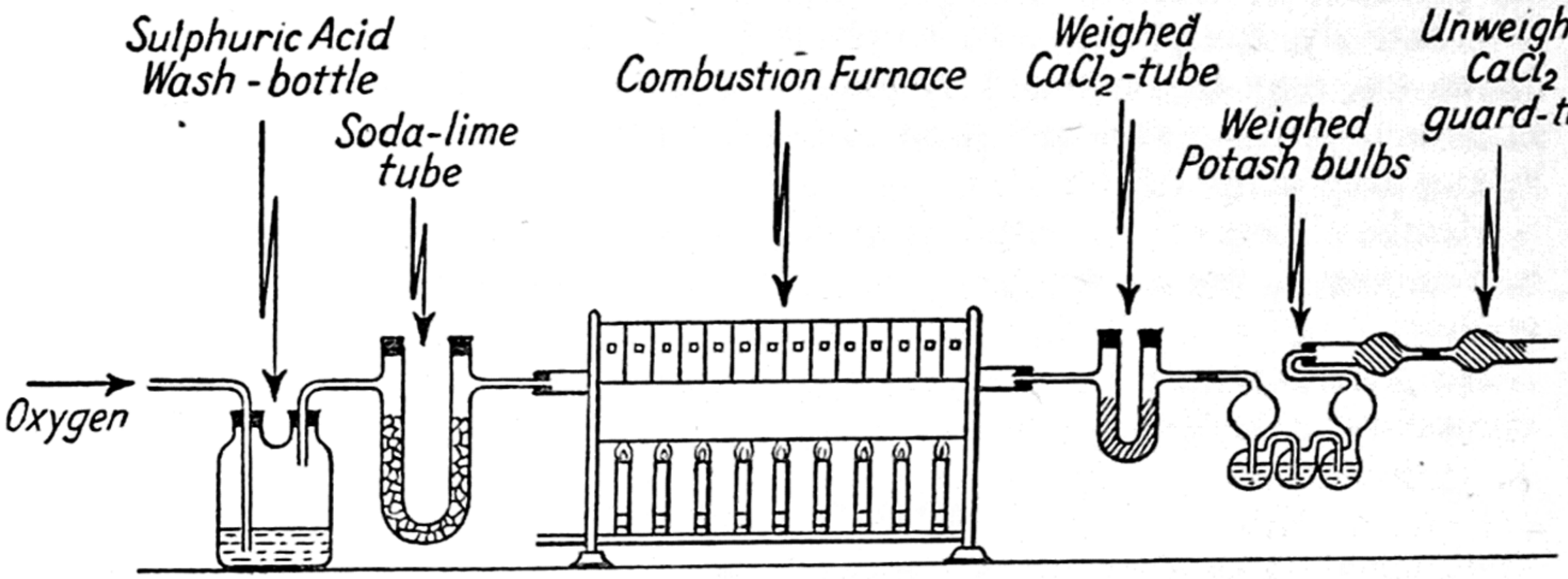


FIG. 274. Apparatus for Determining Carbon and Hydrogen

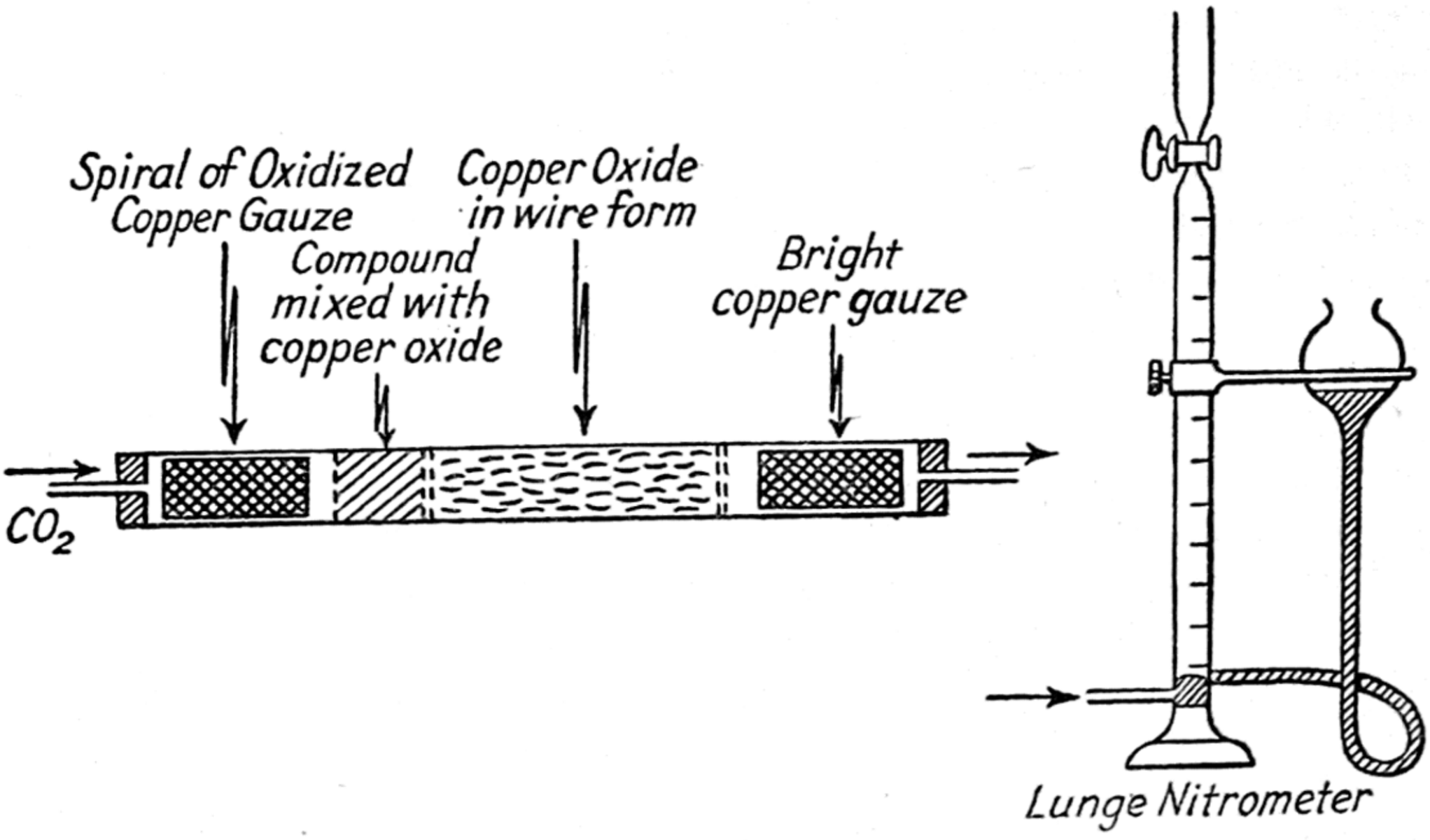


FIG. 275. Combustion Tube for Nitrogen with Lunge Nitrometer

current of pure carbon dioxide in the presence of copper oxide. Any oxides of nitrogen formed are decomposed by a heated copper spiral. The carbon dioxide and nitrogen issuing from the combustion tube are passed through a strong solution of potassium hydroxide to remove the carbon dioxide and the volume of the residual nitrogen then measured in a nitrometer, as shown in Fig. 275.

Kjeldahl Method. In this method a known weight of the organic compound is heated with concentrated sulphuric acid, a little potassium sulphate (to raise the boiling point) and a trace of selenium as catalyst until the compound has been completely decomposed and the nitrogen converted into ammonium sulphate. The solution is then made alkaline and the ammonia distilled over into an excess of a standard solution of acid. The quantity of ammonia is then found by back-titration.

Halogens. The usual method for halogens is *Carius' method.* A known weight of the substance is heated with fuming nitric acid and silver nitrate in a sealed tube. After cooling, the tube is opened and the silver halide subsequently filtered off, dried and weighed. Although the method is simple in principle, it takes rather a long time, requires some experience in sealing and opening the tubes if breakages or even explosions are to be prevented.

Sulphur. Sulphur is also estimated by Carius' method. A known weight of the substance is heated in a sealed tube with fuming nitric acid. The sulphur is oxidized to sulphuric acid which is subsequently estimated as barium sulphate.

Oxygen. No general method is available for estimating oxygen in an organic compound. The percentage of oxygen is always found by difference, that is by subtracting the percentages of all the other elements present from one hundred.

Determination of the Empirical Formula. A knowledge of the percentage composition of the organic compound now enables the empirical formula of the compound to be determined. The procedure is best illustrated by considering a specific example.

(*a*) Percentage composition: C = 40·00, H = 6·67, and O (by difference) = 53·33.

That is, 100 gms of the compound contain: 40 g carbon, 6·67 g hydrogen, and 53·33 g oxygen.

(*b*) The number of gramme-atoms of C, H and O in 100 g of the compound is now found by dividing each of these numbers by the appropriate atomic weights—

$$\text{100 g contain} \begin{cases} 40{\cdot}00 \div 12 = 3{\cdot}33 \text{ gramme-atoms of carbon} \\ 6{\cdot}67 \div 1 = 6{\cdot}67 \text{ gramme-atoms of hydrogen} \\ 53{\cdot}33 \div 16 = 3{\cdot}33 \text{ gramme-atoms of oxygen} \end{cases}$$

That is, the compound is composed of atoms of carbon, hydrogen and oxygen in the ratio: 3·33:6·67:3·33, or more simply 1:2:1. This *simplest*

whole-number ratio of the numbers of the different atoms gives the empirical formula $C_1H_2O_1$, that is CH_2O. The true molecular formula is then given by $(CH_2O)_n$, where n is a small whole number.

Determination of the Molecular Formula. To determine n in the above expression, it is necessary to determine the molecular weight of the compound. If the compound volatilizes at a relative low temperature without decomposition, the simplest method is to determine its vapour density by either the Victor Meyer, Hofmann or Dumas methods (*see* Chapter 2). Other methods include the cryoscopic methods, for example Rast's method which uses camphor as the solvent, or for organic acids and bases the following chemical methods—

(*a*) *Organic Acids.* A weighed amount of the silver salt is heated until it is completely decomposed to leave a residue of metallic silver. If the acid is n basic, then the following reaction where H_nX is the formula of the acid will have occurred—

$$Ag_nX \text{ heated} \rightarrow nAg$$

$$\therefore \quad \frac{\text{Weight of silver salt}}{\text{Weight of silver}} = \frac{108n + X}{108n}$$

Since the formula of the acid is H_nX, a knowledge of X gives the required molecular weight of the acid as $(n + X)$.

(*b*) *Organic Bases.* The amines form insoluble chloroplatinates which on heating decompose to leave a residue of metallic platinum. The amine is therefore dissolved in hydrochloric acid, and a solution of platinic chloride added to precipitate the platinichloride—

$$2CH_3NH_2 + H_2PtCl_6 \rightarrow (CH_3 \,.\, NH_3)_2PtCl_6 \downarrow$$

or, more generally, $$2B \rightarrow (BH)_2PtCl_6 \downarrow .$$

A weighed quantity of the platinichloride is then strongly ignited and the residual platinum weighed—

$$(BH)_2PtCl_6 \rightarrow Pt$$

It follows, therefore, that—

$$\frac{\text{Weight of salt}}{\text{Weight of platinum}} = \frac{2B + H_2PtCl_6}{Pt} = \frac{2B + 410}{195}$$

so that the molecular weight of B, the amine, can be determined.

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